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Interface control in the laser MBE growth of hafnium oxide

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Abstract

High-k hafnium oxide thin films were deposited on p-type (100) silicon substrate by laser molecular beam epitaxy (LMBE) technique, and these ultrathin gate dielectric films were characterized by Auger electron spectroscopy (AES), capacitance–voltage ($C-V$) and current–voltage ($I-V$) measurements. In order to take full advantages of high dielectric constant of HfO_2, the growth of low dielectric constant interfacial layer must be controlled as thin as possible in the deposition process under optimized conditions. The effect of the critical factor of oxygen partial pressure was studied in the range of 2×10^{-3} to 7×10^{-6} Torr while keeping other experimental parameters constant. It was found that by lowering down the oxygen partial pressure to an optimized level, the growth of the low-k interfacial layer was effectively suppressed. A two-step deposition method was adopted to further reduce the thickness of this interfacial layer. The interfacial reaction was better controlled by using this two-step deposition method, resulting in high quality ultrathin HfO_2 films on Si with desired and improved dielectric properties.

Keywords: Hafnium oxide; Gate dielectrics; Interface control; Laser molecular beam epitaxy

1. Introduction

The aggressive scaling of CMOS transistors in recent years has necessitated the search for a suitable high-k gate dielectric to replace the conventional SiO_2 that has a low dielectric constant of ~3.9 [1]. A variety of high-k materials, such as HfO_2, ZrO_2, Al_2O_3, $HfSi_xO_y$, HfO_xN_y and $HfAl_xO_y$, has been considered as the potential good candidates for alternative gate dielectrics [2–4]. Among these alternative high-k dielectric materials, HfO_2 has been regarded as the most promising alternative gate dielectric to replace the currently used SiO_2 for several reasons, such as its high dielectric constant of about 20–30, large energy band gap of ~5.68 eV, and reasonably high tunneling barrier height of >1 eV for both electrons and holes [2]. Various thin film fabrication techniques have been attempted to deposit the HfO_2 thin films on silicon substrate, including metal organic chemical vapor deposition (MOCVD), atomic layer deposition (ALD), pulsed laser deposition (PLD), sputtering, etc. [5–9]. Since neither Hf nor HfO_2 can effectively block the oxygen diffusion, oxygen ions in the processing environment or in the hafnium oxide thin film can easily reach the Si surface, interact with it, and form the undesirable low-k layer at the interface between the substrate and high-k HfO_2 dielectric film. Therefore, in most cases, a considerably thick low–k layer usually exists at the HfO_2/Si interface, which will largely increase the equivalent oxide thickness (EOT) and default the significance of scaling down for CMOS transistors [8–10]. In recent research development, numbers of methods or techniques have been tried by many researchers to suppress the formation of this low-k interfacial layer. Low temperature deposition is one of methods attempted [8,11], however, also it generally results in a relatively low dielectric constant and the poor leakage current property. Thus, how to effectively suppress the formation of this low-k layer in

Table 1
Fabrication of HfO_2 films in different oxygen partial pressure ambient

Sample	Oxygen partial pressure (sccm/Torr)	Argon gas flow (sccm)	Deposition pressure (Torr)
A1	$30/2\times10^{-3}$	0	2×10^{-3}
A2	$3/2\times10^{-4}$	20	2×10^{-3}
A3	$0.3/2\times10^{-5}$	22	2×10^{-3}
A4	$0.1/7\times10^{-6}$	22.2	2×10^{-3}

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Table 2
Structure of the HfO_2/Hf stacks

Sample no.	B1	B2	B3	B4	B5	B6	B7	B8
Hf (nm)	0	1	2	3	4	3	3	3
HfO_2 (nm)	4	4	4	4	4	6	13	18

the deposition process is a challenging issue in alternative high-k dielectric materials for Si CMOS and for nanoelectronics applications.

In this paper, we report our recent research work and experimental results on the ultrathin HfO_2 films with EOT of 1.4 nm deposited by the laser molecular beam epitaxy (LMBE) technique and its high-k value of ~20 by suppressing the formation of the interfacial low-k layer. The effect of oxygen partial pressure in LMBE chamber and a two-step deposition scheme on HfO_2 film growth and properties are also presented and discussed.

2. Experimental

HfO_2 films were deposited onto (100) p-type silicon wafers with resistivity of 1–10 Ω cm using the KrF excimer LMBE technique. The RCA-cleaned wafers were immediately loaded into the LMBE deposition chamber. During the deposition, the power density of the laser beam with wavelength of 248 nm was fixed at 1.8 J/cm^2 and the laser pulse repetition rate was 2 Hz. Either Hf or HfO_2 films were deposited by the ablation from a hafnium target with purity of 99.5%. The effect of oxygen partial pressure during the deposition process in the LMBE chamber on the formation and growth of the interfacial low-k layer was studied by fabricating a set of 15-nm-thick HfO_2 films at 500 °C under different oxygen partial pressure as listed in Table 1. A two-stage deposition method was adopted in this work to further suppress the formation of this low-k interfacial layer and to improve the film properties of the high-k dielectric HfO_2 layer. In this two-step deposition scheme, a hafnium metal layer was first deposited onto the Si substrate in an ultrahigh vacuum of 8×10^{-9} Torr at 200 °C; and then, the substrate temperature was raised to 500 °C and HfO_2 film was subsequently deposited onto the Hf layer in Ar/O_2 ambient while keeping the optimized oxygen partial pressure at 2×10^{-5} Torr. Two batches of HfO_2/Hf stacked samples were prepared to investigate the effect of this two-stage deposition scheme, as listed in Table 2. In the first batch of samples, the thickness of the HfO_2 was fixed at 4 nm while varying the thickness of the buried Hf layer from 0 to 4 nm (Samples: B1–B5); for samples in the second batch, thickness of the buried Hf layer was fixed at 3 nm while the HfO_2 thickness was varied from 6 to 18 nm (Samples: B6–B8). Post-deposition annealing (PDA) was performed ex situ in a rapid thermal annealing (RTA) chamber at 500 °C for 30 s in N_2 ambient with residual O_2. Since oxygen ions can penetrate through both Hf and HfO_2, Hf layer was oxidized into HfO_2 during the annealing [8]. Pt top electrode was deposited at room temperature using an RF magnetron sputtering system. The films were patterned using the lift-off lithography with an active area of 1×10^{-4} cm^2. Finally, the backside of the wafer was etched and deposited with aluminum to form an ohmic contact.

Auger electron spectroscopy (AES) was performed in a JEOL FE–Auger system (Model: JAMP 7800F). The depth profiles were obtained by alternating Ar ion etching with the AES analyses in order to ensure that the surface analysis at each depth were identical for all elements observed. The Ar sputter rate was 2.5 nm/min during the AES depth profile. An HP4284A Precision LCR meter was used to perform the C–V measurement and an HP4155B semiconductor parameter analyzer was used to measure the I–V behavior.

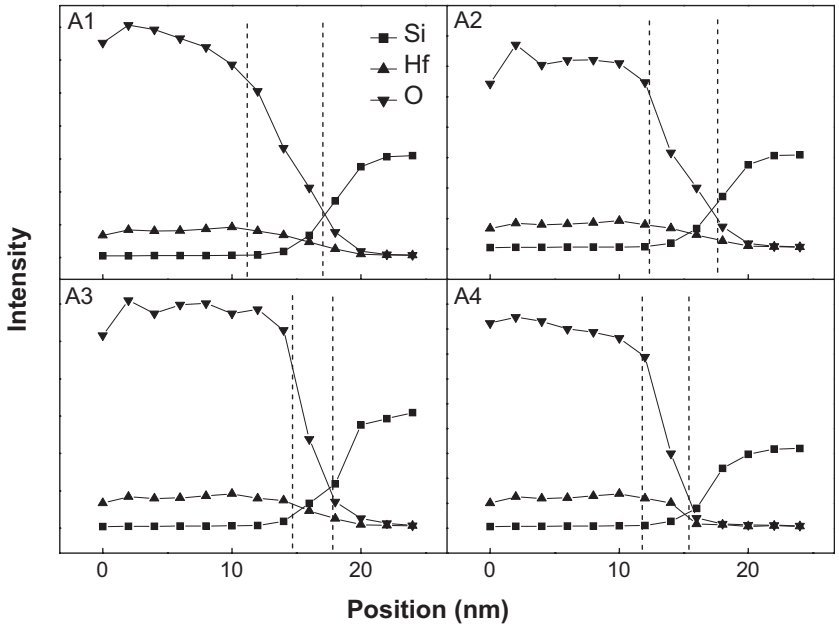

Fig. 1. AES depth profiles of the HfO_2/Si films deposited at different oxygen partial pressures.