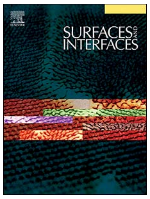
Surfaces and Interfaces 9 (2017) 51–57

Contents lists available at ScienceDirect

Surfaces and Interfaces

journal homepage: www.elsevier.com/locate/surfin



Elemental diffusion study of Ge/Al_2O_3 and $Ge/AlN/Al_2O_3$ interfaces upon post deposition annealing

Yunna Zhu[a], Xinglu Wang[a], Chen Liu[b], Tao Wang[c], Hongyan Chen[c], Wei-Hua Wang[a], Yahui Cheng[a], Weichao Wang[a], Jiaou Wang[b], Shengkai Wang[d], Kyeongjae Cho[a,e], Hui Liu[a,*], Hongliang Lu[c,*], Hong Dong[a,*]

[a] Department of Electronics and Tianjin Key Laboratory of Photo-Electronic Thin Film Device and Technology, Nankai University, Tianjin 300350, China
[b] The Institute of High Energy Physics (IHEP), Chinese Academy of Sciences, Beijing 100049, China
[c] State Key Laboratory of ASIC and System, School of Microelectronics, Fudan University, Shanghai 200433, China
[d] Key Laboratory of Microelectronics Devices & Integrated Technology, Institute of Microelectronics of Chinese Academy of Sciences (IMECAS), Beijing 100029, China
[e] Department of Materials Science and Engineering, The University of Texas at Dallas Richardson, Texas 75080, USA

ARTICLE INFO

Keywords:
ALD
AlN passivation
Ge-oxides
Ge diffusion
Synchrotron radiation

ABSTRACT

The thermal stability of Ge/Al_2O_3 and $Ge/AlN/Al_2O_3$ stacks has been systematically studied upon post deposition annealing (PDA) at 400, 500 and 600 °C with nitrogen gas flow. X-ray photoelectron spectroscopy (XPS) with the incident photon energy of 1486.7 eV and synchrotron radiation photoemission spectroscopy (SRPES) with the incident photon energy of 720, 500 and 200 eV have been used to characterize the interface chemistry and the diffusion of Ge-oxides. More aggressive “clean-up” effect takes place with a higher substrate temperature during the atomic layer deposition (ALD) process for the growth of Al_2O_3 and AlN thin films. A competitive process among the Ge-oxides growth at the Ge/high-k dielectrics interface, the Ge-oxides diffusion, and GeO desorption has been suggested upon PDA treatments. The effective suppression for formation of Ge-oxides by an ultrathin AlN layer has been observed for the samples before PDA and after PDA at 400 °C. Ge-oxide diffusion in proximity to the gate oxide surface has been characterized from the $Ge2p_{3/2}$ spectra by XPS after PDA at 400 °C for Ge/Al_2O_3 and $Ge/AlN/Al_2O_3$ stacks. The diffusion mechanism is hypothesized by diffusion of oxygen vacancy. Moreover, a significant desorption of GeO occurs after PDA at 600 °C for the AlN passivated sample.

1. Introduction

As the aggressive scaling of the metal oxide semiconductor field effect transistor (MOSFET), Si based devices have approached close to the physical limit due to quantum tunneling effect, resulting in unacceptable power consumption [1,2]. To meet the requirement of device scaling, new physics, materials and device structures have been widely explored [3–5]. Compared with Si, Ge is a promising alternative candidate at the sub 10 nm technology node because of its high carrier mobility (both in electron and hole mobility), which can significantly lower the power consumption of the devices [4,5]. Moreover, Ge has already been utilized in strain engineering as SiGe, and it is easy to transform from Si based devices to Ge based devices, in terms of fabrication cost and technology challenge, compared with other high mobility materials, e.g. III-V compound semiconductors [6]. However, the thermodynamically unstable and soluble Ge-oxides become a main challenge for the achievement of high performance Ge based devices [7,8]. The Ge-oxides at the Ge/high-k dielectrics interface associated with high-k oxides deposition and/or post deposition annealing (PDA) process are correlated with interface traps [9,10]. Moreover, Ge-oxides diffusion into the high-k dielectrics and thermal desorption of GeO from the Ge/high-k dielectrics interface upon the PDA process were reported by Secondary Ion Mass Spectrometry (SIMS) study [11]. It is also reported that the GeO volatilization results in the deterioration of the interface quality, which follows the enhancement of leakage current and charge trapping, degrading stability and reliability of the devices [9,11].

Many surface passivation treatments, such as the interfacial nitridation [12,13], the insertion of an ultrathin Si layer [14], sulfur passivation [14] and GeO_2 passivation [15,16], have been reported to improve the electrical characteristics of the devices. Among these passivation methods, ultrathin GeO_2 layer has been considered one of the most promising strategies. Zhang et al. has developed plasma post oxidation method to form ultrathin GeO_x passivation layer at Ge/Al_2O_3

---

[*] Corresponding authors.
E-mail addresses: liuhui@nankai.edu.cn (H. Liu), honglianglu@fudan.edu.cn (H. Lu), donghong@nankai.edu.cn, donghong03@hotmail.com (H. Dong).

http://dx.doi.org/10.1016/j.surfin.2017.07.006
Received 29 January 2017; Received in revised form 29 June 2017; Accepted 27 July 2017

interface by exposing the Ge/Al_2O_3 structures to oxygen plasma and obtained excellent electrical performance [17,18]. Nitridation, such as GeON [19,20], AlN [12,13] passivation layers at the interface, are beneficial to the reduction of interfacial trap density (D_{it}), providing a relatively high quality interface and improving the electrical performance of the device. Li et al. has proposed a Ge/GeO_2/AlN stack model and the AlN layer can passivate the interfacial layer without introducing extra interfacial defects [21]. Therefore, AlN is prone to improve the performance of the Ge/GeO_2/Al_2O_3 stack.

PDA treatment is an important process during the device fabrication, which can reduce D_{it} for Si based devices [22]. Moreover, for nanoscale transistors, the self-heating effect has been reported during operation, which pushes high thermal budget for the Ge/high-k dielectric interface, with respect to the reliability of the devices [23–25]. Therefore, the exploration of the interface chemistry and the elemental diffusion of Ge/high-k dielectric stacks after PDA process is urgent.

The Ge diffusion behavior studies in Ge/GeO_2 system have been widely reported [7,8,26]. However, few work for the Ge diffusion behavior for Ge/high-k dielectrics system has been reported. Shibayama et al. and Chellappan et al. have reported desorption of Ge-oxides from the Ge/Al_2O_3 (1 nm of Al_2O_3) interface during the PDA process, but 1 nm of Al_2O_3 is too thin to capture the Ge-oxides diffusion behavior upon PDA process [27,28]. In this work, the detailed interface characterization by monochromatic XPS (Al kα_1 line, 1486.7 eV) and synchrotron radiation photoemission spectroscopy (SRPES) at the incident photon energy of 720, 500, 200 eV has been carried out on Ge/high-k dielectrics stacks with thick (~4 nm) high-k oxide films to systematically study the elemental diffusion upon PDA at 400, 500 and 600 °C for both the Ge/Al_2O_3 and the Ge/AlN/Al_2O_3 stacks.

2. Experimental

2.1. Material and methods

Three gallium doped *p*-type Ge (100) samples were split from the same 2″ single crystal wafer provided by MTI Corporation. All samples were initially degreased by isopropyl alcohol (IPA) in ultrasonic for 30 s and then blow dry by ultrahigh purity nitrogen gas (99.999%) in this study. Then the ultrathin Al_2O_3 and AlN layers were grown by atomic layer deposition (ALD) in a Benneq TFS-200 reactor. For the growth of Al_2O_3 thin film, Trimethylaluminum (TMA) and deionized water vapor (DIW) were used as the metal precursor and the oxidant precursor, respectively. On the other hand, for the growth of AlN thin layer, TMA and ammonia were used as the precursors. 30 cycles of Al_2O_3 were deposited on Group A samples by sequential TMA/Purge/DIW/Purge of 0.2 s/3 s/0.2 s/3 s at the substrate temperature of 300 °C; 10 cycles of AlN by sequential TMA/purge/NH_3/purge of 0.2 s/3 s/0.2 s/3 s at the substrate temperature of 360 °C, followed by 20 cycles of Al_2O_3 at 300 °C (the same recipe as Group A) were deposited on Group B samples; 30 cycles of Al_2O_3 were deposited on Group C samples at 360 °C, with the same recipe as Group A. The detailed process of the samples is shown in Table 1. The Al_2O_3 layer on Group A samples is ~4.6 nm, and the Al_2O_3 layer + AlN layer is ~4 nm (AlN layer is less than 1 nm). The thickness of the high-k dielectric film is estimated by the attenuation of XPS signal (Ge 3*d* spectrum) after the ALD process through X-ray photoelectron spectroscopy (XPS). The calculation process is shown in Supplementary Material (Formula S1 and S2). *Ex situ* PDA treatments at 400, 500 and 600 °C were carried out for Group A samples and Group B samples in ultrahigh purity N_2 gas (99.999%) flow for 1 min with the gas flow rate of 400 SCCM. To avoid the evaporation of the Ge-oxides from cleaved Ge surface (without Al_2O_3 coverage) during the PDA process, all samples were cleaved prior to ALD to make sure the Ge sample is uniformly coated by high-k dielectrics. This will rule out the sublimation of Ge from the cleaved surfaces.

Table 1
Process for Each Group (× Indicates Process Not Applied).

Group	Treatment	No PDA sample	PDA samples
Group A	IPA	Ge/Al_2O_3(300 °C)	400 °C 500 °C 600 °C
Group B	IPA	Ge/AlN(360 °C)/Al_2O_3(300 °C)	400 °C 500 °C 600 °C
Group C	IPA	Ge/Al_2O_3(360 °C)	× × ×

2.2. Characterization

For XPS characterization, PHI 5000 was used, which is equipped with a 16 channel hemispherical analyzer operating at a pass energy of 46.95 eV in constant analysis energy mode for core level spectra scans. The XPS spectra were taken at 45° for the analyzer with respect to the sample surface. For SRPES characterization, the samples were carried out on beam line 4B9B in the Institute of High Energy Physics (IHEP), Chinese Academy of Sciences. The pass energy for the hemispherical analyzer is 20 eV and the analyzer was normal to the sample surface. SRPES spectra were taken at different incident photon energies (hυ = 720, 500, 200 eV). Ge 2$p_{3/2}$ spectra were characterized by XPS. The Ge 3*d* core level spectra were characterized by both XPS and SRPES. The branching ratio for the Ge 3*d* core level spectra is 0.677 and the doublet splitting is 0.57 eV in this work. To compensate the band bending effect and partial charging effect, the Ge 3$d_{5/2}$ spectra of Ge bulk peak were referenced to 29.3 eV [29] The 1+, 2+, 3+ and 4+ states are separated from the Ge bulk peak, with the energy shift of 0.95, 1.9, 2.95, 3.75 eV, respectively [30]. The consistent fitting parameter was applied to all Ge 3*d* spectra in this study.

2.3. Calculation

A mathematical model is established to quantify the diffusion length as well as the quantity of Ge-oxides (in the following paragraph), which takes advantage of the exponential decay nature of the photoemission signal with different incident energies. For the Ge crystal, the lattice constant *a* is 0.5654 nm. Effective attenuation length (EAL) of photoelectrons for Ge 3*d* in Ge bulk and the high-k dielectrics is denoted as λ_1 and λ_2, respectively. EAL was estimated following the database provided by NIST [31]. λ of photoelectrons for Ge 3*d* at different incident energy is shown in Supplementary Material (Table S1). Assuming all Ge-oxides are in one atomic layer and distribute evenly away from the interface. The thickness of Al_2O_3 is d_2 (nm) and the distance of Ge-oxides layer to sample surface is d_1 (nm). Then the distance of Ge-oxides to the sample interface is Δd (d_2-d_1). The atomic density of each atomic layer of Ge-oxides atoms in high-k dielectrics is n_1; the atomic density of each atomic layer of Ge atoms in the Ge bulk is n_2; the parameter of incident X-ray is f_i, which takes into account of the spot size, the geometry of the incident X-ray, and sample area exposed to the detector. I_{Ge} represents the theoretical intensity from the Ge substrate (Formula 1), and $I_{Ge\text{-}O}$ represents the intensity of the Ge-oxides (Formula 2). The intensity of Ge-oxides and Ge bulk obtained from measurement is denoted as A and B at 1486.7 eV, C and D at 720 eV, respectively. The detailed intensity is shown in Supplementary Material (Table S2). The intensity ratio R is defined by Formula 3. According to Formula 4, Δd is determined by R from the photoemission measurement, which shows the higher the R, the smaller the Δd. According to the calculation model, R, Δd and Concentration (intensity ratio of Ge-oxides to the corresponding bulk peak for Ge 3*d* spectra) as a function of PDA is calculated for the quantitative analysis. The results are shown in Tables 2 and 3.

$$\begin{aligned} I_{Ge} &= \sum_{m=0}^{\infty} n_2 f_i \times e^{-\frac{d_2}{\lambda_2 \sin\theta}-\frac{ma}{4\lambda_1 \sin\theta}} \qquad \text{where } m = 0,\ 1,\ 2,\ 3\cdots\cdots \\ &= n_2 f_i \times e^{-\frac{d_2}{\lambda_2 \sin\theta}} \Big/ \left(1 - e^{-\frac{a}{4\lambda_1 \sin\theta}}\right) \end{aligned} \quad (1)$$