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Interface chemistry and electronic structure of ALD-derived HfAlO/Ge gate stacks revealed by X-ray photoelectron spectroscopy

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A B S T R A C T

In this article, the effect of annealing temperature on the electronic structure and interface chemistry of HfAlO/Ge gate stack grown by atomic layer deposition (ALD) have been investigated systematically. Based on characterization from x-ray photoelectron spectroscopy (XPS), the evolution of electronic structure and interface chemistry of HfAlO/Ge gate stacks as functions of annealing temperature been detected. With increasing the annealing temperature from 500 to 600 °C, crystallization of HfAlO gate dielectrics has been observed. Annealing the samples on 700 °C leads to the reduction of HfAlO component and the formation of Al_2O_3, which brings about the improved interface stability. The optimized interface chemistry related to annealing temperature indicates the potential application for HfAlO gate dielectrics in future Ge-based microelectronic device.

1. Introduction

The functionality and performance of the integrated circuit depends on the increasing number of transistors, which result from the rapid shrinking of the device dimensions such as channel length and gate dielectric thickness of the transistor. With the continued scaling, the charge scattering of Si-based MOSFET has lead to the mobility degradation in high-k gate dielectric and metal gate. As a result, Ge-based MOSFET with high-k gate dielectric is one of the attractive approaches that has been widely investigated due to its higher carrier mobility than its Si counterpart and good thermodynamic stability, and easier integration of Ge on Si [1–3]. However, Ge-based MOS device suffers severe degradation of the electron mobility and the regressive electrical performance due to the high density of interface state traps close to the conduction-band edge at the Ge/high-k interface, which comes from the absence of a good thermally-grown oxide on the Ge substrate [4]. Therefore, the investigation of suitable high-k gate dielectrics is necessary to minimize the oxides formation and eliminate the Fermi level pinning effect [5,6]. By far, many high-k gate oxides have been chosen as the potential candidates as gate dielectrics for Ge-based MOSFET devices, such as HfO_2 oxides, which is essential component in aggressively scaled Ge-MOSFETs due to their ability of increasing the gate switching voltage and suppressing the gate leakage current. However, HfO_2 has low crystallization, poor barrier to oxygen diffusion and poor thermal stability under high temperature, which limit its potential application in Ge-based MOSFETs [7,8]. Compared with HfO_2 gate dielectrics, HfAlO alloy retains amorphous up to 1000 °C [9], suggesting that HfAlO gate dielectric thin films have higher crystallization temperature and higher thermal ability compared with HfO_2. Besides, it is specified that annealing temperature can lead to the generation of HfAlO alloy. Meanwhile, the breakout of the bond of Hf–Al–O and the formation of Al–O will benefit the performance optimization of Ge-based MOSFET device [10]. And the Al_2O_3 is an effective barrier to oxygen diffusion and prevent the formation of low-k interfacial layer.

By now, many deposition methods have been pursued to deposit Hf-based high-k gate dielectrics on Ge substrates, such as co-sputtering, sol-gel, and metal-organic chemical vapor deposition (MOCVD), atomic-layer-deposition (ALD), and so on. Among those methods, ALD method has several advantages over other deposition techniques in obtaining high-k gate dielectrics with excellent

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dielectric quality as well as accurate thickness and component control ability. Although there are some investigations of the interface chemistry of ALD-derived HfAlO gate dielectrics, few work has been carried out to investigate the annealing temperature dependent interfacial stability and the phase separation of ALD-derived HfAlO on Ge substrate. In current work, annealing temperature dependent interface chemistry of HfAlO/Ge gate stacks grown by ALD has been studied by means of characterization from x-ray photoelectron spectroscopy. Meanwhile, the interfacial stability and bonding states of HfAlO/Ge gate stack as a function of annealing temperature has been determined in details.

2. Experimental

Commercially purchased *n*-type Sb-doped (100)-oriented Ge wafers with resistivity of 0.04 Ω cm cleaved from the same wafer were used as the deposition substrates in current work. Prior to loading the wafers into the ALD chamber, all the wafers were degreased by dipping in methanol solution for 5 min at 75 °C for the sake of removing organic contamination and other impurity ions. Then, all wafers were put into a mixed solution ($NH_3\cdot H_2O$:H_2O = 1:4) and cleaned by buffered HF solution for 30s to remove the surface oxides. Finally, all wafers were followed by rinsing with de-ionized water and drying with N_2. Then the samples were immediately transferred to an ALD chamber (LabNano 9100, ENSURE NANOTECH). In current work, the precursors for HfO_2 were terakis (ethymethylamino) hafnium (TEMAH) and H_2O, while the trimethylaluminum (TMA) and H_2O were the precursors of Al_2O_3. TMA and TEMAH were contained in bubbler and delivered into the reaction chamber by high pure nitrogen. The growth temperature and the base pressure for ALD chamber during deposition were controlled at 200 °C and 1.0 torr, respectively. A typical ALD growth cycle for HfO_2 was 1s TEMAH pulse/3s N_2 purge/0.3s H_2O pulse/2s N_2 purge and 0.5s TMA pulse/2s N_2 purge/0.5s H_2O pulse/2s N_2 purge for Al_2O_3. Firstly, HfO_2 film with 2 cycles was prepared. Secondly, Al_2O_3 film with 1 cycle was deposited, followed by two cycles of HfO_2 film. Totally, 20 cycles have been carried out to obtain HfAlO gate dielectrics with thickness of 6 nm. In order to investigate the effect of annealing temperature to the interfacial stability of HfAlO/Ge gate, all the samples were processed by rapid thermal annealing (RTA) with a temperature range of 500–700 °C in high vacuum ambient condition (6.3×10^{-5} mbar) for 60 s. The gate dielectric film thickness was obtained by *ex-situ* spectroscopic ellipsometry (SC630, SANCO Co, Shanghai, SE) analysis. All the measurements were carried out in air at room temperature in the wavelength range of 280–1100 nm with a step of 10 nm at incident angles of 65° and 75°. And Cauchy-Urbach model was used to obtain the thicknesses. Additionally, ex-*situ* x-ray photoelectron spectroscopy (XPS) measurements were performed to study the impact of the annealing temperature dependent interface chemistry and phase separation of HfAlO gate dielectrics on Ge substrate. Here, Thermo Fisher Scientific XPS (ESCALAB 250Xi) system is equipped with monochromatic Al K_α source (1486.6 eV) under a base pressure of 2.1×10^{-9} Torr and a hemispherical analyzer with a pass energy of 20 eV. Narrow scans with a step of 0.05 eV and pass energy of 20 eV were performed for 20 times for binding energy of specific elements. The charge neutralizations of x-ray bombarded samples are performed by flood guns. The C 1s line with a binding energy of 284.8 eV was used as a reference to eliminate the charging effect. The software (XPSPEAK Version 4.1) was used for XPS fitting.

3. Results and discussion

The core level survey spectra and corresponding chemical composition of the as-deposited and annealed HfAlO gate dielectrics measured by XPS have been displayed in Fig. 1. All characteristic peaks derived from Hf, Al, O, and Ge elements as well as a small amount of C component coming from air contamination have been observed. The determination of interface chemistry of Ge/high-k gate stack is very important for choosing the suitable high-k gate dielectrics for CMOS application. As we know, the interface stability depends on the annealing temperature. To obtain the information from the interface and investigate the evolution of the chemical bonding states of HfAlO/Ge gate stacks as a function of annealing temperature, Ge 3d, O 1s, Hf 4f, and Al 2p XPS core-level spectra were examined nondestructively using XPS. Fig. 2 demonstrates Al 2p core-level spectra of the as-deposited and annealed samples at 500, 600 and 700 °C, respectively. Based on Fig. 2, it can be noted that the peak coming from the as-deposited located at the binding energy of 74.82 eV may be attributed to the Al–O bonds in Al_2O_3. Annealing the sample at 500 °C leads to the shift of the peak towards a lower binding energy of 74.33 eV, which is in good agreement with the value for HfAlO reported by Suri [11], indicating that annealing treatment at 500 °C brings about the chemical reaction of $HfO_2/Al_2O_3/HfO_2$ gate stacks and accelerates the formation of composited HfAlO alloy. With increasing the annealing temperature from 500 to 600 °C, the Al spectra shows two peaks centered at binding energies of 74.9 and 74.3 eV, respectively, which can originate from Al–O and Hf–Al–O bonding states. Based on the evolution of Al 2p XPS spectra at 600 °C, it can be concluded that annealing at 600 °C results in the partial breakage of the Hf–Al–O bonding state and the formation of Al–O component, indicating that the phase separation has occurred. After annealing at 700 °C, only one peak located at 74.8 eV has been observed, indicating that HfAlO has fully transferred into HfO_2 and Al_2O_3 and the phase separation process of HfAlO have finished.

Annealing temperature dependent Hf 4f XPS core-level spectra for as-deposited and annealed samples have been demonstrated in Fig. 3. Based on Fig. 3, both peaks, attributed to the Hf $4f_{7/2}$ and Hf $4f_{5/2}$ bonding states separated by almost 1.5 eV, have been detected. As shown in Fig. 3(a), two separated Hf 4f peak located at 17.31 and 18.89 eV corresponds to the Hf $4f_{7/2}$ and Hf $4f_{5/2}$ peaks of HfO_2, suggesting the existence of $HfO_2/Al_2O_3/HfO_2$ laminated structure. Annealing the sample at 500 °C, the shift of Hf 4f binding energy towards higher energy side has been observed, which may be due

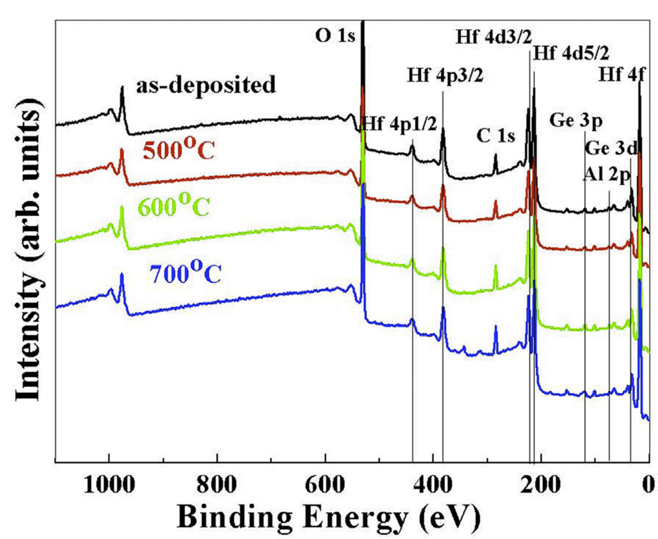

Fig. 1. Core level XPS survey spectra of the as-deposited and annealed HfAlO gate dielectrics with different annealing temperatures.