Dependence of Band Alignment and Interfacial Suboxide GeOx Thickness of Thermal GeO2/Ge Stacks on GeO2 Thickness by X-ray Photoelectron Spectroscopy

X. L. Wang1,*, S. K. Wang2,*, J. Zhang3, W. W. Wang1, H. G. Liu1, J. Yan1, C. Zhao1, D. P. Chen1, T. C. Ye1

1Key Laboratory of Microelectronics Devices & Integrated Technology, 2Microwave Device and IC Department
3Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, China

Phone: +86-10-82995508, E-mail: wangwenwu@ime.ac.cn (W. W. Wang), liuhonggang@ime.ac.cn (H. G. Liu)

*These two authors contributed equally to this work

Abstract

The band discontinuity and interfacial suboxide GeOx of thermal GeO2/Ge stacks are investigated by X-ray photoelectron spectroscopy (XPS) on various thicknesses of GeO2 on Ge substrate. The band structure of GeO2/Ge stacks is found to be GeO2 thickness dependent with the variation range of band offset being ~0.8 eV, while the thickness of GeO2 is GeO2 thickness independent. The physical origin of this dependence is attributed to the distribution of the gap states and fixed charges across the whole stacks.

1. Introduction

Ge is a promising channel material for further improving CMOS performance thanks to its intrinsic high electron and hole mobility. The poor high-k/Ge interface, however, is a challenging issue to realize the Ge CMOS technology.1,2 GeO2 has been reported to passivate the Ge surface effectively with low Dg of ~1011 cm-2.3,4 The energy band structure of GeO2/Ge stacks is rather important for controlling and improving the performance of CMOS gate stacks. The band offset result at GeO2/Ge interface, however, is still in debate with large scattering in the range of ~1 eV.5,18

In this paper, the band discontinuity of thermal GeO2/Ge stacks is investigated by using X-ray photoelectron spectroscopy (XPS) on various thicknesses of GeO2 on Ge substrate. The band structure of GeO2/Ge stacks is found to be GeO2 thickness dependent and possible origins are demonstrated. The thickness of GeOx suboxide between thermal GeO2 and Ge is found to be GeO2 thickness independent.

2. Experimental

After wet cleaning of p-Ge, GeO2 was thermally grown at 550 °C with four different thicknesses, which were calibrated by spectroscopic ellipsometer (SE). The XPS were recorded using Thermo Scientific ESCALAB 250Xi equipped with a monochromatic Al Kα radiation source of 1486.8 eV and with pass energy of 15 eV. The energy scale was calibrated by setting the binding energy of GeSSub as the exponential attenuation factor. The larger the binding energy difference between core-levels of GeO2 and Ge substrate ΔBE(Ge 3dGeO2-Ge 3dGe Sub). It can be seen that ΔBE(Ge 3dGeO2-Ge 3dGe Sub) is GeO2 thickness dependent with the variation range of ~0.2 eV. Fig. 1 also gives the XPS spectra of Ge 2p1/2 of GeO2/Ge stacks with four different thicknesses of GeO2. Also shown in Table I is the Ge 2p1/2 binding energy of GeO2 by fitting the corresponding spectra. The binding energy difference between Ge 2p1/2 of GeO2 and Ge 3d5/2 of Ge substrate ΔBE(Ge 2pGeO2-Ge 3dGe Sub) is shown in Fig. 2. It can be seen that ΔBE(Ge 2pGeO2-Ge 3dGe Sub) is also GeO2 thickness dependent with the variation range of ~0.8 eV, which is very large.

The Ge 2p1/2 to valence band maximum (VBM) distance of GeO2 can be experimentally determined to be 1248.08 eV, and the Ge 3d5/2 to VBM of Ge is 29.13 eV as shown in Fig. 3. The band gap of GeO2 is determined to be 5.9 eV based on the SE method, which is not shown here. Then the valence and conduction band offsets (VBO and CBO) of GeO2/Ge stacks can be calculated and schematically shown in Fig. 4 for different thicknesses of GeO2 on Ge. It can be concluded that the band offset of GeO2/Ge stacks is GeO2 thickness dependent and displays jagged variation. In addition, Fig. 5 shows the intensity ratio of suboxide GeOx to Ge substrate. It can be seen that the ratio is nearly constant, indicating that the thickness of GeOx is identical and independent on the GeO2 thickness.

The reason why the Ge 2p1/2 but not the Ge 3d is selected for GeO2 to determine the band alignment is as follows; the XPS is a weighted average of the detected signals underneath the surface with the inelastic mean free path as the exponential attenuation factor. The larger the binding energy of core-level is, the nearer to the surface the position of the detected core-level is selected to represent the surface information. The different variation trends of ΔBE(Ge 3d3/2GeO2-Ge 3d5/2Sub) and ΔBE(Ge 2pGeO2-Ge 3dGe Sub) are due to different detected positions for the Ge 3d and 2p.

The interesting dependence on GeO2 thickness of the band offset of GeO2/Ge stacks is discussed. Here we consider the following cases; (1) only consider the interfacial gap states (IGS) at GeO2/Ge interface. Then the VBO is...
GeO₂ thickness independent; (2) consider the IGS and the fixed interfacial positive charges (FIPC) at GeO₂/Ge interface. Then the VBO decreases with GeO₂ thickness; (3) consider the IGS and FIPC at GeO₂/Ge interface and bulk charges (BC) in GeO₂, then the VBO decreases with GeO₂ thickness; (4) consider the IGS and BC, the VBO is independent on the GeO₂ thickness. As a result, the jagged dependence of band offset on GeO₂ thickness cannot be explained by considering the above cases. These indicate that another new effect should be considered. Here we argue that the gap states (GS) on the GeO₂ surface contribute to this jagged variation of the band offset. Based on our previous work, if the charge neutrality level of GS on GeO₂ surface is higher that the Fermi level at GeO₂/Ge interface, the VBO increases with thicker GeO₂. Consequently, the jagged dependence of band offset on the GeO₂ thickness is attributed to the combination of IGS and FIPC at GeO₂/Ge interface, BC in the GeO₂ and SGS on the GeO₂ surface.

4. Conclusions
The band offset of GeO₂/Ge extracted by XPS method is found to be GeO₂ thickness dependent while the GeO₂ thickness shows no dependence on the GeO₂ thickness. The large variation range of ~0.8 eV for band offset of GeO₂/Ge, which is not the experimental error, indicates the important influences of gap state distributions and various charges across the GeO₂/Ge stacks, and the decouple of these parameters is essential to obtain the actual band offset just at the GeO₂/Ge interface.

Acknowledgments
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References

Table I Summary of the binding energy of core-level peaks.

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<th>Thickness of GeO₂ (nm)</th>
<th>Ge 3d⁵/₂ Ge Sub. (eV)</th>
<th>Ge 3d⁵/₂ GeO₂ (eV)</th>
<th>Ge 2p₁/₂ GeO₂ (eV)</th>
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<tr>
<td>4.6</td>
<td>3.33</td>
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<td>5.5</td>
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<td>6.9</td>
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<td>9.3</td>
<td>3.30</td>
<td>1223.07</td>
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Fig. 1 XPS spectra of Ge 3d and Ge 2p₁/₂ of GeO₂/Ge stacks with four different physical thicknesses of GeO₂.

Fig. 2 Dependence on the GeO₂ thickness of the ΔBE(Ge 3d⁵/₂ GeO₂-Ge 3d⁵/₂ Ge Sub.) and ΔBE(Ge 2p₁/₂ GeO₂-Ge 3d⁵/₂ Ge Sub.). Two different variation trends are observed.

Fig. 3 XPS spectra of 9.3 nm GeO₂/Ge stacks to determine the Ge 2p₁/₂ to VBM distance of GeO₂ and the Ge 3d⁵/₂ to VBM distance of Ge.

Fig. 4 Energy band offset diagram of GeO₂/Ge stacks of four different thicknesses of GeO₂.

Fig. 5 Intensity ratio of GeOₓ to Ge, which is extracted by the Ge 3d core-level spectrum in Fig. 1.