Effect of precursor entrance sequence during atomic layer deposition on the Al_2O_3/Ge interface by X-ray photoelectron spectroscopy

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The effect of precursor entrance sequence during atomic layer deposition (ALD) on the chemical and electronic characteristics of Al_2O_3/Ge interface is investigated by X-ray photoelectron spectroscopy (XPS). The trimethylaluminium (TMA) or H_2O precursor is first introduced into the chamber to grow Al_2O_3 dielectric on cleaned Ge. An abrupt Al_2O_3/Ge interface without interlayer is obtained for both cases. The valence band offset (VBO) at the Al_2O_3/Ge interface becomes, however, smaller when the TMA precursor is first introduced. This is due to the lower charge neutrality level (CNL) of gap states at Al_2O_3/Ge interface which is induced by the TMA treatment of Ge surface.

~2.6 μm Ge film was first epitaxially grown on n-Si. After wet cleaning of the Ge surface, 6 nm Al_2O_3 film was grown by ALD using TMA and H_2O as precursors at 300 °C. Two different growth modes were employed as follows; one mode was that during the ALD growth H_2O precursor was first introduced into the chamber (denoted as H_2O-first). The other mode was that the TMA was first introduced (denoted as TMA-first). Then 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.

Fig. 1 shows the XPS spectra of Ge 3*d* and Al 2*p* core-levels of 6-nm-Al_2O_3/Ge stacks for the two growth modes of Al_2O_3. It can be seen that signals only from Ge substrate are detected without formation of GeO_2 or GeO_x for both growth modes, indicating that abrupt interface is obtained. The value indicated in the figure presents the Al $2p_{3/2}$ to Ge $3d_{5/2}$ core-level distance. Fig. 2 shows the XPS spectra of Ge 3*d* and valence band (VB) of 6-nm-Al_2O_3/Ge stacks, and Fig. 3 shows the Al 2*p* and valence band of 10-nm-Al_2O_3/Ge stacks. The values in the figure show the core-level to valence band maximum (VBM) distance for Ge and Al_2O_3, respectively. Then the VBO of Al_2O_3/Ge stacks can be calculated to be 3.83 eV and 3.96 eV, respectively, for TMA-first and H_2O-first Al_2O_3/Ge stacks. Fig. 4 schematically shows band structure of the two mode Al_2O_3/Ge stacks.

The smaller VBO of TMA-first Al_2O_3/Ge stacks compared with that of H_2O-first Al_2O_3/Ge stacks is explained. Based on our previous work,[1] gap states appear not only at the Al_2O_3/Ge interface but also on the surface of Al_2O_3 as shown in Fig. 5(a). The electron transfer between these gap states, which is determined by the relative positions of CNLs of these gap states, induces potential drop across the whole stacks to align the Fermi levels of Al_2O_3 and Ge as shown in Fig. 5(b). The smaller VBO of TMA-first Al_2O_3/Ge stacks indicates that the energy band of Al_2O_3 bends upward compared to that of H_2O-first Al_2O_3/Ge. So if the CNL of gap states at Al_2O_3/Ge interface after TMA-first treatment becomes lower, the energy band of Al_2O_3 will bend more upward to balance the Fermi levels of the stacks, resulting in smaller VBO of Al_2O_3/Ge stacks. These means that the precursor entrance sequence during ALD growth can alter the electronic properties of Al_2O_3/Ge interface.

[1] X. L. Wang, J. J. Xiang *et al.*, APL **102**, 041603 (2013).

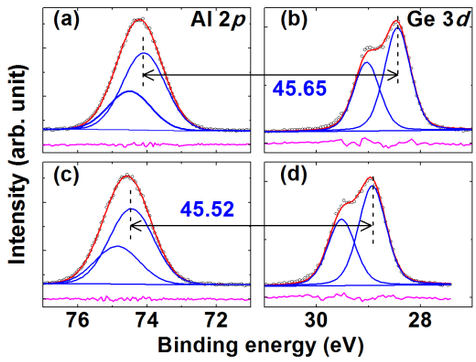

Fig. 1 XPS spectra of Al 2*p* and Ge 3*d* for (a)-(b) H_2O-first and (c)-(d) TMA-first Al_2O_3/Ge stacks.

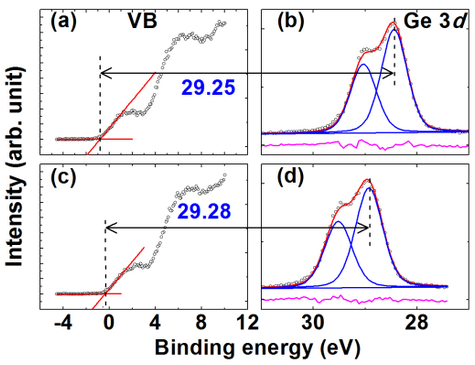

Fig. 2 XPS spectra of Ge 3*d* and VB for (a)-(b) H_2O-first and (c)-(d) TMA-first Al_2O_3/Ge stacks.

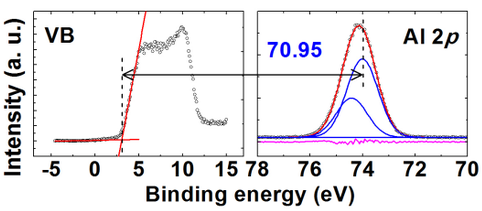

Fig. 3 Spectra of Al 2*p* and VB of 10-nm-Al_2O_3/Ge stacks.

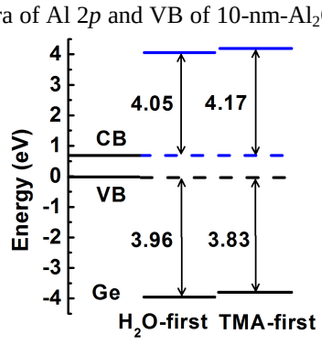

Fig. 4 Schematic diagram of band alignment of the two mode Al_2O_3/Ge stacks. Here the band gap of Al_2O_3 and Ge are taken to be 8 and 0.67 eV, respectively.

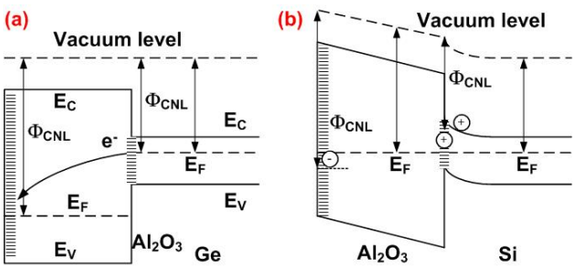

Fig. 5 Schematic diagram of band structure of Al_2O_3/Ge stacks (a) before contact and (b) after contact. Gap states appear on the Al_2O_3 surface and at Al_2O_3/Ge interface. electrons transfer from Al_2O_3/Ge interface to Al_2O_3 surface to align the Fermi levels or namely CNLs.