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Study on Al_2O_3/Ge interface formed by ALD directly on epitaxial Ge

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Abstract

Germanium (Ge) has been attracting considerable attention as a high mobility channel material to enhance the performance of CMOS circuits. One of the most important issues for realization of practical Ge-MOSFET devices with superior performances is requirement to improve qualities of gate dielectric/Ge interfaces. In this work, Al_2O_3/Ge structures are fabricated by direct atomic layer deposition (ALD) on epitaxialy grown Ge. We indicate that ALD incubation time is fully suppressed by the ALD on a completely clean Ge surface created by Ge epitaxy on a Ge substrate. Moreover, x-ray photoelectron spectroscopy analyses reveal that unintentional formation of a GeO_2 at the Al_2O_3/Ge interface can be almost avoided by the ALD on the epitaxial Ge whereas the interfacial GeO_2 layer is present for samples exposed to the air before ALD. These results clearly indicate that direct ALD on epitaxial Ge is a very promising method to significantly improve Ge MOSFET performances.

Keywords: Germanium, Al_2O_3, MBE, ALD, XPS

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent years, Ge has drawn considerable attention as a high-mobility channel material toward next-generation complementary metal-oxide-semiconductor (CMOS) circuits. In particular, by inducing strain into Ge, highly enhanced mobilities which greatly exceed the bulk mobility have been reported [1, 2]. One of the most critical requirements for practical applications of Ge MOS devices is the formation of high-quality gate stacks and interfaces between a gate insulator film and a Ge surface. As next generation gate insulators, high-k gate materials have been intensively studied for applications to not only Si but also non-Si metal-insulator-semiconductor (MIS) structures, such as GaAs [3–6] and Ge [7–16]. A number of studies have been reported to date in order to realize high quality interfaces comparable to that of Si/SiO_2, and low D_{it} has been achieved by inserting GeO_2 at an interface between the Ge and an Al_2O_3 film deposited by atomic layer deposition (ALD) [12–14].

Commonly, a gate insulator film, such as Al_2O_3, is deposited on a Ge surface after chemical wet-cleaning of the Ge wafer. Unlike a Si surface, however, a good quality hydrogen-terminated surface cannot be obtained for the Ge after a HF dip treatment, causing the Ge surface to be contaminated. Therefore, it is considered that further improvements of the quality of the interface between the Al_2O_3 film and the Ge surface is still important in order to achieve lower D_{it}. To completely avoid this contamination, we firstly attempt the deposition of the Al_2O_3 film with ALD directly on epitaxially grown Ge by molecular beam epitaxy (MBE), where both MBE and ALD chambers are vacuum-connected so that samples can be transferred without being exposed to the atmosphere. As a result of the direct ALD on the epitaxial Ge, we obtain drastic improvements of interfacial properties of Al_2O_3/Ge.

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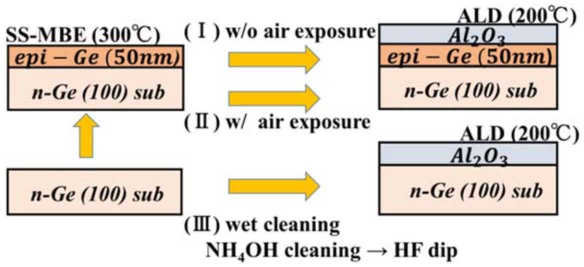

Figure 1. Sample fabrication processes. (I) ALD Al_2O_3 on epi-Ge without air exposure, (II) ALD Al_2O_3 on epi-Ge with air exposure and (III) ALD Al_2O_3 on wet-cleaned Ge substrate.

Table 1. Summary of samples, processes and ALD cycles.

Sample	Process	Cycle
A	I	200
B	III	200
C	I	20
D	II	20

2. Experiments

The sample fabrication procedure is illustrated in figure 1 and samples are summarized in table 1. An n-type Ge (100) substrate was used in this study. The Ge substrate was chemically cleaned with NH_4OH solution and followed by a HF dip and de-ionized water rinse. For process (I), the wet-cleaned Ge substrate was loaded into an MBE chamber and subjected to thermal cleaning at 600 °C for 10 min. Subsequently, a 50 nm thick Ge layer (called epi-Ge hereafter) was homo-epitaxially grown on the Ge substrate at 300 °C. The epitaxial growth of Ge was carried out with a solid source MBE system with a Ge effusion cell. The as-grown sample was subsequently transferred to the vacuum-connected ALD chamber and an Al_2O_3 film was deposited by ALD. For comparison, two other processes (II) and (III) were separately fabricated. For process (II), after the epitaxial growth of the Ge, the sample was once taken out from the chamber and exposed to the atmosphere for 5 min. The sample was then reloaded into the ALD chamber and an Al_2O_3 film was deposited. For process (III), the wet-cleaned Ge substrate was loaded into the ALD chamber and an Al_2O_3 film was deposited without the Ge epitaxy. ALD of Al_2O_3 films was carried out for 20 or 200 cycles with precursors of TMA and H_2O at a substrate temperature of 200 °C. Here, one cycle is defined as a period including TMA gas flow for 3 s., H_2O gas flow for 3 s. and purge for 10 s. A spectroscopic ellipsometer was used to estimate the deposited Al_2O_3 film thickness. Chemical bonding states were examined by x-ray photoelectron spectroscopy (XPS). The radiation source was AlKα (1486.6 eV) and the take-off angle (TOA) was 15°, 21°, 30°, 52° or 90°. The photoelectron spectra of Al 2*p* and Ge 3*d* were measured.

3. Results and discussion

First, to evaluate effects of the epi-Ge insertion on the ALD thickness, samples with sufficiently thick Al_2O_3 films were characterized. Thicknesses of the Al_2O_3 films were estimated by spectroscopic ellipsometry measurements for samples A and B which have Al_2O_3 films deposited with 200 cycles ALD. An obtained thickness was 64 nm for sample B, which was subjected to ALD after wet cleaning. In contrast, the thickness of 122 nm was obtained for the sample A, where the ALD was performed after the Ge epitaxy. It is found that for sample B, which has no Ge epitaxial growth prior to ALD, an onset of the Al_2O_3 film deposition is markedly delayed. This is known as an incubation time for ALD. On the other hand, for sample A with the epi-Ge, such deposition delay is hardly observed and the film thickness begins to increase from the initial cycles of the ALD. This is presumably because OH groups are easily bonded to dangling bonds which can remain only on the clean epitaxial Ge surfaces.

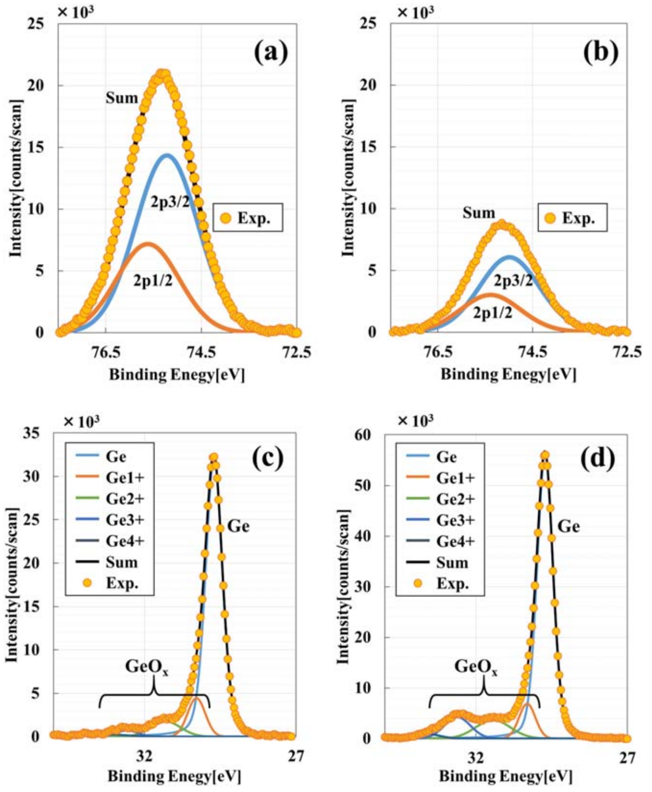

Figure 2. (a), (b) Al 2*p* and (c), (d) Ge $3d_{5/2}$ photoelectron spectra measured at TOA of 21° for the sample C ((a), (c)) and the sample D ((b), (d)).

Next, the difference in the deposition delay is observed for the samples with thin Al_2O_3 films. XPS measurements were performed for samples C and D on which the Al_2O_3 films were deposited for 20 ALD cycles. Figures 2(a) and (b) show Al *2p* XPS spectra obtained with take-off angle (TOA) of 21° for samples C and D, respectively. Intensities of Al *2p* peaks coming from the Al_2O_3 films are significantly lower for sample D than C, reflecting that the deposition delay occurs for sample D similarly to sample B. Due to the exposure of the epitaxially grown Ge surface to the atmosphere, it can be seen that the Al_2O_3 ALD delay takes place as in the wet cleaned surface (sample B). This is thought to be due to natural oxidation of the epi-Ge during exposed to the atmosphere.

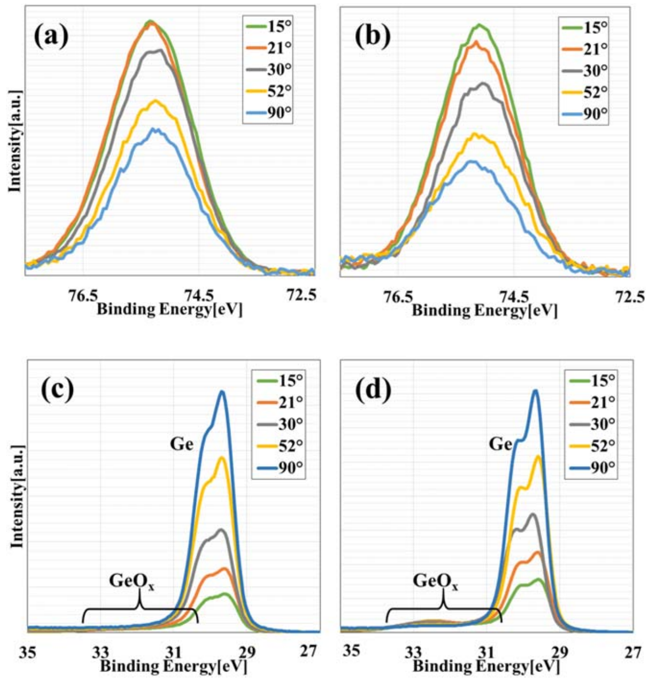

Figure 3. (a), (b) Al 2p and (c), (d) Ge 3d photoelectron spectra at various TOA for the sample C ((a), (c)) and the sample D ((b), (d)).

In order to investigate interface properties in detail, Ge 3$d_{5/2}$ spectra were measured as shown in figures 2(c) and (d) for samples C and D, respectively. Here, only the Ge 3$d_{5/2}$ component was calculated with the energy difference between Ge 3$d_{3/2}$ and Ge 3$d_{5/2}$ being 0.58 eV [17, 18] and the intensity ratio being 2:3. It is found that the peaks related to GeO$_x$ are smaller for sample C than D. In particular, a Ge^{4+} peak caused by GeO$_2$ [18, 19] is hardly observed for sample C, indicating that the oxidation of Ge is almost suppressed by ALD on the epi-Ge without exposure to the air. Note that other GeO$_x$ peaks are considered to be associated with Al$_2$O$_3$ and Ge interface. On the other hand, larger peaks coming from GeO$_x$ including GeO$_2$ is observed for sample D, which means that the epi-Ge is oxidized during air exposure and the oxidized Ge remains after the ALD of the Al$_2$O$_3$ layer. When comparing Ge substrate peak intensities, sample D exhibits a higher peak intensity than sample C. Since the TOA is relatively small (21°) and the signal is more surface sensitive, the observed higher Ge peak for sample D means that the Ge is closer to the surface for sample D than C. This indicates that the thickness of the Al$_2$O$_3$ layer is larger for sample C than D, which agrees well with ellipsometry measurement results.

Next, results of angle resolved XPS measurements for samples C and D are shown in figure 3. Photoelectrons are attenuated by inelastic scattering in the film. Therefore, information on a sample surface is more dominant when the take-off angle (TOA) is small, and information on a deeper region of the sample begins to appear when the TOA becomes large. From figure 3, it is found that the peak intensity of Al 2p increases as the TOA decreases. In the case of Ge 3d, the relationship between the TOA and the peak intensity is the opposite to Al 2p. These results indicate that the layer involving Al exists on the top of another layer with Ge.

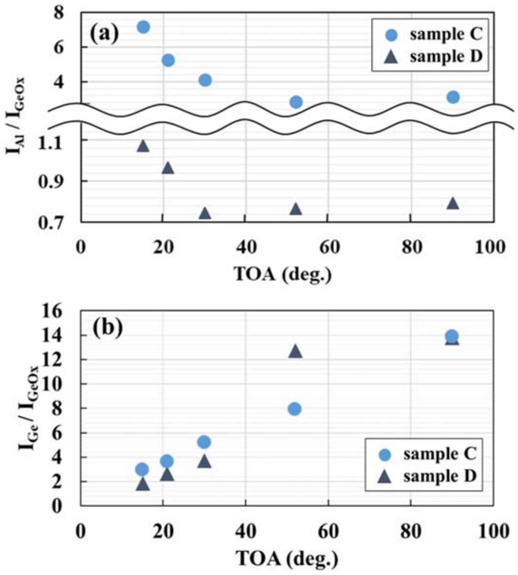

Figure 4. TOA dependence of the peak area intensity ratios of (a) the Al and (b) Ge peaks to the GeO$_x$ peak for sample C and sample D.

The photoelectron spectra shown in figure 3 were analyzed in more detail, and TOA dependences of each peak intensity ratios were obtained as shown in figure 4. Each peak intensity was normalized by the intensity of GeO$_x$ peaks (the sum of peaks Ge^{1+} $\sim$ Ge^{4+}).

Figure 4(a) shows the intensity ratios I_{Al2p}/I_{GeOx} for samples C and D. For both samples, the intensity ratio I_{Al2p}/I_{GeOx} increases with decreasing TOA. From these behaviors, it can be said that Al (Al$_2$O$_3$) exists over GeO$_x$ in both samples. Moreover, the value of I_{Al2p}/I_{GeOx} for sample C is much larger than that for D, corresponding to the fact that the Al$_2$O$_3$ thickness is thicker and GeO$_x$ peaks are smaller for sample C than those for sample D as described above. Figure 4(b) shows the intensity ratios I_{Ge}/I_{GeOx} for samples C and D. Contrary to the I_{Al2p}/I_{GeOx} cases, it is found that the ratios I_{Ge}/I_{GeOx} increases with the TOA increases for both structures. This indicates that GeO$_x$ is formed over the Ge substrate. To summarize the results above, it was demonstrated that both samples consist of stacks of Al$_2$O$_3$/GeO$_x$/Ge (sub).

4. Conclusions

In order to form a high quality Al$_2$O$_3$/Ge interface, Ge was epitaxially grown on the Ge substrate using MBE and then Al$_2$O$_3$ was deposited by direct ALD method without exposing the sample to the atmosphere by transfer in vacuum. As is well known, ALD deposition delay was observed when Al$_2$O$_3$ was deposited on wet-cleaned Ge substrate and when the epitaxial Ge was subjected to air exposure. On the other hand, when ALD was performed on the epitaxial Ge without air exposure, almost no deposition delay was observed. In addition, it was shown by XPS measurements that formation of oxidized Ge is markedly suppressed by the direct ALD on the epitaxial Ge. From the above results, it is expected that the high-quality Al_2O_3 film can be formed on a completely cleaned Ge surface by this method, and it will be possible to further increase the performance of Ge MOSFETs by improving interface characteristics.

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