Aluminum Nitride for Ge-MIS Gate Stacks with Scalable EOT

T. Tabata^{1,2}, C. H. Lee^{1,2}, T. Nishimura^{1,2}, K. Nagashio^{1,2}, and A. Toriumi^{1,2}

¹ Department of Materials Engineering, The University of Tokyo, ² JST-CREST 7-3-1 Hongo, Bunkyo, Tokyo 113-8656, Japan Phone and Fax: +81-3-5841-7161, E-mail: tabata@adam.t.u-tokyo.ac.jp

1. Why aluminum nitride (AlN) on Ge?

EOT scaling is still challenging in Ge-MIS gate stacks, because GeO₂ interface-layer (IL) is required for maintaining its high channel mobility [1,2]. It means the lower processing temperature is required for suppressing the GeO desorption, while a high temperature process (~600°C) will be desirable when device stability and reliability are considered. Therefore, to make a good interface on Ge at a high temperature, non-oxide insulator will fundamentally be demanded. Nitrides seem to be one of promising candidates, because IL increase in N2-PDA will not be observed below 650°C thanks to no reaction. Issues to be considered are k-value, band-gap (band-offsets), and interface stability and reliability on Ge. From this viewpoints, aluminum nitride (AlN) will be a strong candidate, because a relatively large energy band-gap (~6 eV) [3] with a medium-k and thermal stability up to ~1300°C without its chemical decomposition [4] have been reported. A few papers have reported relatively good interface properties in AlN/Ge stacks [5,6], however, details of the interface reaction with Ge have not been understood well.

In this paper, we report physical and electrical properties in AlN/Ge MIS gate stacks and discuss the possibility of Ge-MIS gate stacks with scalable EOT.

2. Experimental

 AIN_x films were deposited on p-type Ge (100) wafers by rf-sputtering of AlN target in N₂. The film thickness was determined by grazing incident X-ray reflectivity (GIXR) measurement and Spectroscopic Ellipsometry (SE). The post-deposition-annealing (PDA) was performed at 600°C for 5 min in N₂. Then, Au and Al were evaporated as the gate electrode and the back ohmic contact, respectively.

3. Results and Discussion

The dielectric constant of as-deposited AIN_x film was confirmed to be k~12 in our Ge MIS capcitors. The optical band-gap of AlN_x film was estimated to be 5.4~5.7 eV on Ge. Fig. 1(a) shows the square of the optical-absorption coefficient, α , of as-deposited 23.9 nm-thick AlN_x film calculated for the direct-gap transition. The more important point is the band offset balance of the conduction with valence band offsets. We experimentally investigated the band alignment of AlN_x/Ge interface by XPS. Fig. 1(b) shows the valence-band spectra of as-deposited 23.9 and 3.2 nm-thick AlN_x film on Ge. The valence band offset at AlN_x/Ge is 2.6~2.7 eV, which means the conduction-band offset is estimated to be 2.34~2.74. Since the charge-up effect (~0.4 eV) on Al2p core-level was actually observed in 23.9 nm-thick AlN_x case, each of the conduction-band and the valence-band offset at AlN_x/Ge interface are 1.94~2.34 eV and 3.0~3.1 eV, respectively. This balanced





and large offsets are beneficial points of AlN_x film on Ge. This is understandable by considering electronic structure origin of AlN. The valence band edge of AlN is mainly derived from the N2p orbital, while it is from the O2p one in typical oxides. In addition, the conduction-band edge in AlN will be enhanced thanks to no d-electron [7]. Therefore, AlN_x has a big advantage against high-k oxides and even nitrides.

For the physical properties, AlN_x seems to be an almost ideal gate insulator on Ge, however, a slight GeN_x formed on Ge surface after sputtering in N₂ is still concern because Ge_3N_4 decomposes associated with the N₂ desorption above ~580°C [8], which may degrade the electrical properties of AlN_x/Ge MIS capacitors from the analogy of the GeO desorption in GeO₂/Ge system [9]. To clarify the N₂ desorption kinetics in more detail, we investigated N₂ desorption. Fig. 2(a) shows the TDS spectra of N₂ desorption from three types of samples such as

- (i) 3 nm-thick $AlN_x/10$ nm-thick GeN_x/Ge
- (ii) 3 nm-thick AlN_x/Ge,
- (iii) 3 nm-thick $AlN_x/10$ nm-thick SiO_2/Si .

No N_2 desorption is observed from the sample (iii) in Fig. 2, indicating that AlN_x is thermally much more stable than Ge_3N_4 . On the other hand, the N_2 desorption is observable



Fig. 2. TDS spectra of the N₂ desorption form (i) 3 nm-thick $AlN_x/10$ nm-thick GeN_x/Ge , (ii) 3 nm-thick AlN_x/Ge , and (iii) 3 nm-thick $AlN_x/10$ nm-thick SiO_2/Si stacks. The heating was performed from room-temperature to 830°C with 20°C/min. Mass number 28 was selected for the detection of N₂ desorpted from the samples.

in the sample (ii). This is possibly due to GeN_x slightly formed on Ge surface in AlN_x sputtering process. In the case of the sample (i) with 10 nm-thick GeN_x layer intentionally inserted between AlN_x and Ge substrate, N₂ desorption intensity is clearly enhanced in a few orders. In the desorption spectra, it is noted that the N_2 desorption consists of two parts. The peak deconvolution was performed in the sample (i). One part is attributable to the tail region which is a slowly varying spectrum, and the other part is to the sharp peak with threshold temperature. The AlN_x thickness dependences of both parts were shown in Fig. 3(a) and (b). The former shows the peak intensity increase with the decrease of AlN_x thickness. This fact possibly means that N₂ desorption is described by the diffusion process driven by the interface reaction, and that the AlN_x film may serve as the capping layer against the N_2 desorption. The latter sharp peak also shows the decrease of threshold temperature with the decrease of AlN_x thickness. The total amount of N_2 desorption calculated from the area of deconvoluted curves, however, is almost the same regardless of AlN_x thickness. Therefore, it is possibly due to the net decomposition of inserted GeN_x layer.

For preparing thin EOT gate stack with AlN_x on Ge, in fact the ultra-thin AlN_x film is needed. But the capping effect of AlN_x for suppressing the N₂ desorption from unintentionally formed GeN_x is weakened in ultra-thin region as shown in Fig. 3. This should cause the interface degradation in AlN_x /Ge MIS gate stacks. To suppress the N₂ desorption, we have applied the high-pressure N₂ (HPN) PDA, which is discussed elsewhere [10]. **Fig. 4** shows the 1MHz bi-directional C-V characteristics of 3.2 nm-thick AlN_x film on Ge annealed at 600°C. Note that the HPN PDA dramatically improves C-V characteristics, while the large interface states are observed in the same gate stack in atmospheric-pressure N₂ (APN) PDA.

4. Conclusions

We studied AlN_x gate stack on Ge. AlN_x film shows k~12 and well-balanced conduction-band offset (1.94~2.34 eV) and valence–band offset (3.0~3.1 eV) on Ge. The N₂ desorption from AlN_x/Ge stacks was also investigated intensively. By thinning AlN_x film, it becomes hard to suppress N₂ desorption. We demonstrated one method to breakthrough this challenge by using the high-pressure N₂ PDA.



Fig. 3. The deconvoluted signals in the TDS spectra of the N_2 desorption form $AlN_x/10$ nm-thick GeN_x/Ge with AlN_x thickness dependence, including (a) the tail region given by the Gaussian function and (b) the sharp peak with threshold temperature given as the residual part after the Gaussian fitting.



Fig. 4. The 1MHz bi-directional C-V characteristics of Au/3.2 nm-thick AlN_x/p -Ge(100)/Al MIS capacitors fabricated by the annealing of 1 atm and 50 atm N₂, processed at 600°C.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research (S) by Japan Society for the Promotion of Science (JSPS). One of the authors (T.T.) was grateful to the support by JSPS Research Fellowships for Young Scientists.

References

- [1] C. H. Lee et al., Tech. Dig. IEDM (2010) p.416.
- [2] R. Zhang et al., Tech. Dig. IEDM (2011) p.642.
- [3] H. Yamashita et al., J. Appl. Phys. 50 (1979) 896.
- [4] Y. Kumagai et al., J. Crystal Growth 305 (2007) 366.
- [5] K. H. Kim et al., Appl. Phys. Lett. 90 (2007) 212104.
- [6] S. J. Whang et al., Tech. Dig. IEDM (2004) p.307.
- [7] G. Lucovsky, J. Non-Cryst. Solids 303 (2002) 40.
- [8] K. Kutsuki et al., Jpn. J. Appl. Phys. 47 (2008) 2415.
- [9] K. Kita et al., Jpn. J. Appl. Phys. 47 (2008) 2349.
- [10] T. Tabata et al., in submission.