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Atomically flat interface formation on Ge (111) in oxidation process

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Abstract

The interface morphology control is indispensable for high performance Ge CMOS. In this work, we demonstrate atomic-level planarization on Ge (111) in thermal oxidation for the first time. We also discuss a possible mechanism of the interface planarization, by paying attention to a difference of oxidation mechanism between Ge and Si. These results indicate an intrinsic advantage of Ge (111) for Ge FETs.

1. Introduction

To realize high performance Ge FETs, particularly at high carrier density region, atomically flat surface of Ge substrate is quite useful [1]. In fact, H_2 anneal is very effective to form atomically flat surface on Ge(100), (110) and (111) [2].

On the other hand, oxidation of Ge is quite different from that of Si which is described by O_2 diffusion in SiO_2 [3,4]. In Ge oxidation, we also have to consider O vacancy (V_o) generation at GeO_2/Ge interface, which is equivalent to Ge oxidation by GeO_2 (GeO_2 + Ge -> $2GeO_2$ + $2V_o$), and V_o diffusion from the interface. Therefore, if the GeO_2 oxidation occurs in the similar manner as H_2 annealing, atomically flat GeO_2/Ge interface might be realized by oxidation process.

In this work, we investigate impacts of oxidation process on morphology of GeO_2/Ge interface and discuss a mechanism of oxidation at GeO_2/Ge interface.

2. Experimental results

Firstly, we analyzed morphology at GeO_2/Ge interface formed by O_2 oxidation. (100), (110), and (111) orientated Ge substrates were cleaned by HF-last process, and oxidized at 550°C in O_2 ambient for 10, 20 and 30 min. The thickness of GeO_2 were estimated to be 18~28 nm by spectroscopic ellipsometry (SE) measurement. Oxidation rate of Ge is in order of (110) > (100) > (111), which is consistent with the result reported by Sasada, et al. [5], and different from Si case. Thermally grown GeO_2 was removed by HF, and then Ge surface was observed by AFM. Although randomly roughened structure was observed on Ge(100) and (110) surfaces in this experimental condition, Ge(111) surface exhibits clear step & terrace structure as shown in **Fig. 1(a)**. The step structure formed on Ge(111) interface exactly corresponds to Ge(111) single step composed of two atomic layers (**Fig. 1(b)**). As far as we know, the atomically flat interface formation of Si in oxidation has never been reported in Si. Of course, the roughness RMS on Ge(111) surface is much improved to be 0.15 nm @ 1 x 1 μm by oxidation.

Next, to simply analyze the impact of Ge oxidation by GeO_2, we also thermally annealed GeO_2/Ge stack in inert gas atmosphere. Almost 70-nm-thick GeO_2 films were stacked by rf-sputtering on chemically cleaned Ge substrates and annealed in N_2 atmosphere at 550°C. The step & terrace structure also appeared only at GeO_2/Ge(111) interface by over 10 min annealing as shown in **Fig. 2(a)**. Furthermore, a relationship between GeO_2 thickness on Ge(100), (110) and (111)

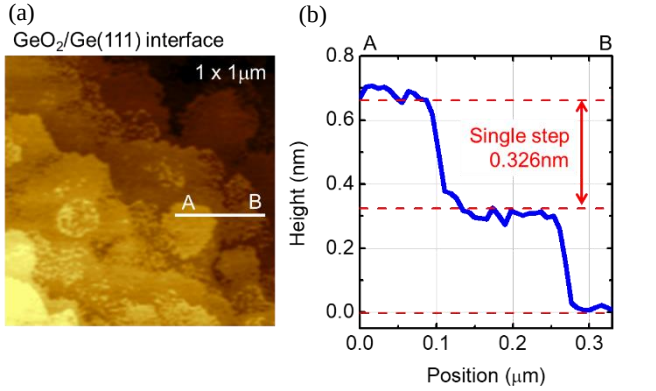

Fig. 1 (a) AFM image of GeO_2/Ge(111) interface oxidized at 550°C for 30 min. Clear step & terrace structure is observed. **(b)** Height profile between A and B points shown in (a). Single step height exactly corresponds to 2 atomic layers in Ge(111). Such a planarization in oxidation is never reported in Si.

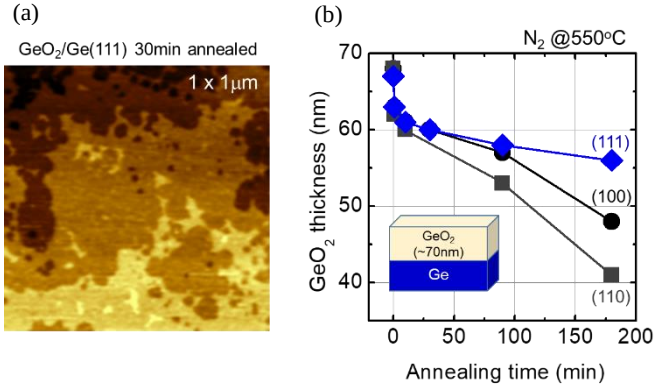

Fig. 2 (a) AFM image of GeO_2/Ge(111) interface annealed in N_2 ambient for 30 min. The trend of surface orientation dependence of oxidation rate and (111) interface planarization are similar to O_2 oxidation case. **(b)** GeO_2 thickness of sputtered GeO_2(~70 nm)/Ge stack annealed at 550°C in N_2 ambient as a function of annealing time. Since reduced GeO_2 thickness corresponds to amount of Ge oxidized by GeO_2, GeO_2 oxidation rate becomes in order of (110) > (100) > (111). Initial rapid reduction might be caused by densification of sputtered GeO_2 film.

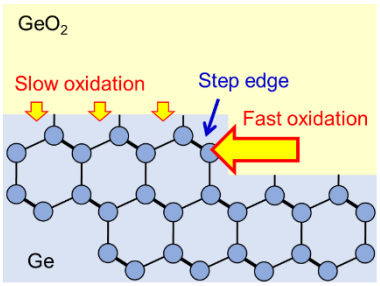

Fig. 3 Schematic image of GeO_2 oxidation at GeO_2/Ge (111) interface. The preferential step edge oxidation is simply described as different oxidation rate in direction to parallel to terrace from that in direction to perpendicular to terrace.

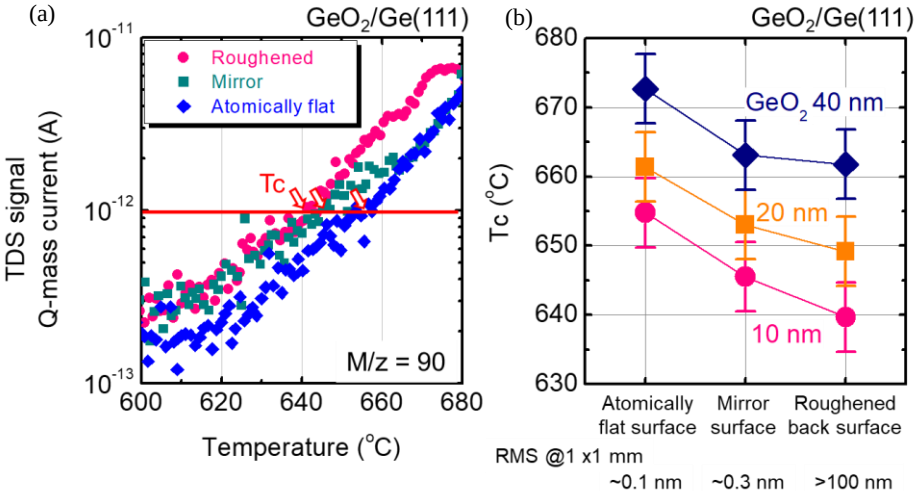

Fig. 4 (a) Typical GeO desorption spectrum from GeO_2(10 nm)/Ge(111) stack measured by thermal desorption spectroscopy and definition of critical temperature (T_c) where GeO desorption rate increase to the value where Q-mass current (M/z = 90) is 1 x10^{-12} A. **(b)** T_c of GeO_2/Ge(111) stacks with various interface roughness (RMS roughness @ 1 x 1 μm: ~0.1 nm (atomically flat surface), ~0.3 nm (mirror surface), >100 nm (roughened back surface)) and GeO_2 thickness. The Tc shifts to higher with decreasing step edge density (decreasing interface roughness).

and annealing time is shown in **Fig. 2(b)**. The order of GeO_2 oxidation rate of (110) > (100) > (111) is in a good agreement with that of O_2 oxidation. So, it is also expected that low O_2 oxidation rate of Ge(111) is mainly caused by GeO_2 oxidation.

3. Discussion

The experimental results indicate that step & terrace structure is easily formed at Ge(111) interface in oxidation process, and suggest that Ge(111) terrace is quite robust against GeO_2 oxidation and step edge is preferentially oxidized as shown in **Fig. 3**. If so, GeO_2 oxidation rate on Ge(111) in initial stage should sensitive to step edge density. We verified step edge oxidation on Ge(111) through GeO desorption triggered by GeO_2 oxidation [6]. To prepare GeO_2/Ge(111) stack with various step edge density at interface, we stacked GeO_2 film by rf-sputtering on Ge (111) substrates with GeO_2 oxidized atomically flat surface, initial mirror surface and roughened back surface. **Fig. 4(a)** shows typical thermal desorption spectroscopy profiles and a definition of critical temperature at which GeO desorption rate in GeO_2/Ge stack increases up to a certain value. As shown in **Fig. 4(b)**, it is obvious that the critical temperature shifts to higher with decreasing step edge density. This result surely supports the preferential oxidation at step edge on Ge(111).

On the other hand, atomically flat interface was not observed on Ge(100) and (110) in this work. Considering the fact that oxidation species in GeO_2 oxidation is GeO_2 by which Ge interface is totally covered, macroscopic parameter like surface energy might be effective to discuss the surface orientation dependence. Since surface energy on Ge surface without reconstruction becomes higher in order of (100) > (110) > (111) [7], it is likely that GeO_2/Ge(100) and (110) interfaces are less stable than GeO_2/Ge(111) interface. Therefore, those interface might be roughened by local GeO_2/Ge(111) interface structure formation. Furthermore, it is speculated that Ge-Ge bonds nearby the interface are oxidation sites and Ge-O-Ge bridge structure is formed by direct O insertion in the site in microscopic view. Therefore, we might also have to consider Ge-Ge bonds configuration around oxidation site in terms of local stress.

GeO_2 based oxide is better for gate stack in Ge CMOS in terms of low interface state density [8], while we have to care that Ge oxidation by GeO_2 is progressed even in thermal process. Therefore, we conclude that Ge(111) is the most favorable surface for Ge CMOS from viewpoints of interface morphology and unintentional additional oxidation.

4. Conclusions

We have demonstrated atomically flat GeO_2/Ge(111) interface by simple heat treatment process for the first time. It is caused by high robustness of Ge(111) terrace against the particular oxidation mechanism of Ge. For Ge CMOS, Ge(111) surface is quite promising in terms of interface morphology and unintentional additional oxidation as well as conduction mass.

Acknowledgements

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