Evaluation of GeO desorption behavior in the metal/GeO₂/Ge structure and its improvement of the electrical characteristics

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The relation between germanium monoxide (GeO) desorption and either improvement or deterioration in electrical characteristics of metal/GeO₂/Ge capacitors fabricated by thermal oxidation has been investigated. In the metal/GeO₂/Ge stack, two processes of GeO desorption at different sites and at different temperatures were observed by thermal desorption spectroscopy measurements. The electrical characteristics of as-oxidized metal/GeO₂/Ge capacitors shows a large flat-band voltage shift and minority carrier generation due to the GeO desorption from the GeO₂/Ge interface during oxidation of Ge substrates. On the other hand, the electrical properties were drastically improved by a postmetallization annealing at low temperature resulting in a metal catalyzed GeO desorption from the top interface. © 2010 American Institute of Physics. [doi:10.1063/1.3452367]

I. INTRODUCTION

Germanium (Ge) is one of the very promising candidates as a channel material for future metal-oxide-semiconductor field-effect transistors (MOSFETs) because of its high carrier mobility. A combination with a high dielectric constant (high- κ) material as a gate insulator film is required for the FETs to obtain a much higher speed and lower power consumption. Similar to the high- κ /Si system which has an interfacial silicon dioxide (SiO₂) layer, an interface layer (IL) is required to maintain a good interface condition for the high- κ /Ge structure. Although Ge dioxide (GeO₂) is one of the solutions for the IL, the interface between GeO₂ and Ge is not stable since Ge monoxide (GeO) is easily desorbed by the following reaction:¹⁻⁵

GeO desorption leads to a critical deterioration of the interface properties such as an increase in interface states and a negative flat-band voltage (V_{FB}) shift. To our knowledge, no researchers have achieved an ideal capacitance-voltage (C-V) curve for as-fabricated metal/GeO₂/Ge capacitors without any special treatments such as high pressure oxidation,⁵ plasma oxidation,^{6,7} vacuum annealing,⁸ or surface nitridation has been reported before.^{9,10} Recently, it has been reported that low temperature annealing of GeO₂/Ge with a cap layer is effective to improve the electrical characteristics.⁵ Thus, one has to consider not only the interface of GeO₂/Ge but that of metal/GeO₂ and GeO₂ bulk as well. In this paper, the relationship between GeO desorption and the improvements in electrical characteristics of metal/GeO₂/Ge capacitors fabricated by thermal oxidation has been investigated.

II. EXPERIMENTAL DETAILS

GeO₂/Ge structures were fabricated by conventional thermal oxidation of HF-last p-type Ge (100) substrates at several temperatures between 400 and 600 °C in a furnace. The thicknesses of the thin GeO₂ films (<7.0 nm) were determined using the intensity ratio between Ge⁰ and Ge⁴⁺ in Ge 3d spectra of x-ray photoelectron spectroscopy (XPS) measurements.¹¹ For GeO₂ thickness above 7.0 nm, it was determined by using capacitance equivalent thickness (CET) calculated using a κ -value of 5.1 for GeO₂. The GeO₂ surface roughness was measured by an atomic force microscope (AFM). For electrical characterization, Al or Au electrodes were formed on the GeO₂ films using conventional vacuum evaporation. After the fabrication of the MOS capacitors, C-V characteristics were measured at 1, 10, 100, and 1000 kHz. GeO desorption was observed by thermal desorption spectroscopy (TDS) under ultrahigh vacuum (UHV, $\sim 10^{-8}$ Pa) conditions. Mass numbers of 86, 88, 89, 90, and 92 were considered as GeO signals. For the TDS measurements, GeO₂/SiO₂/Si stacks were also fabricated.

III. RESULTS AND DISCUSSION

A. GeO₂/Ge interface

First, GeO desorption characteristics of thermally oxidized GeO₂/Ge stacks at 500 °C were investigated by annealing either under UHV conditions or atmospheric pressure in N₂. Figure 1 shows the TDS signal of GeO desorbed from GeO₂(10 nm)/Ge by UHV annealing at ~ 700 °C. The results clearly show that GeO desorbs at temperatures above 400 °C under UHV condition. The GeO₂ layer was fully eliminated after the TDS anneal evident from the steep drop in the curve. The inset shows the GeO₂ thickness as a function of the N₂ annealing time of GeO₂(6.5 nm)/Ge at 400–600 °C at 1 atm. To measure the GeO₂ thickness exactly, XPS has been used for this measurement. When an-

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FIG. 1. (Color online) TDS spectrum of GeO desorbed from $\text{GeO}_2(10 \text{ nm})/\text{Ge}$. GeO was volatilized above 400 °C under UHV conditions. The inset shows GeO_2 thickness vs time of N_2 annealing of $\text{GeO}_2(6.5 \text{ nm})/\text{Ge}$ at 400–600 °C. The decreasing GeO_2 thickness indicates that GeO is also volatilized during annealing under atmospheric pressure above 400 °C in N_2 .

nealing at 500 and 600 °C, the GeO_2 thickness decreased with the annealing time due to the GeO desorption from the GeO_2/Ge interface.

Here, our main interest was the GeO desorption behavior during the course of the GeO_2 growth. To explain the behavior, thermally oxidized Si was positioned 0.5 mm above the bare Ge substrates during the oxidation at various temperatures between 400 and 550 °C, as shown in Fig. 2(a). GeO that desorbs during the GeO_2 formation adsorbs to the SiO_2 surface. Note that for each temperature the obtained thickness of the GeO_2 films formed on the Ge substrates was $\sim 10 \text{ nm}$. Oxidation times are 5, 20, 100, and 1000 min at 550 °C, 500 °C, 450 °C, and 400 °C, respectively. After the oxidation of the Ge substrates, the SiO_2 surface was ex-

FIG. 2. (Color online) (a) A schematic diagram of this experiment. Thermally oxidized Si was set $\sim 0.5 \text{ mm}$ above Ge substrates during the thermal oxidation of Ge at various temperatures. SiO_2/Si adsorbed the GeO which desorbed from the GeO_2/Ge interface. (b) XPS Ge 3d spectra of SiO_2 surfaces as a function of oxidation temperature. Ge^{4+} peaks were clearly observed from SiO_2 surface annealed above 450 °C. There were no peaks in the 400 °C oxidation. These results indicate that GeO is also volatilized during thermal oxidation of Ge substrates above 400 °C. The inset shows an expanded spectrum of the 400 °C oxidation.

amined using XPS. XPS Ge 3d spectra of the SiO_2 surface are described in Fig. 2(b). Ge^{4+} peaks are clearly observed in the results obtained from samples oxidized above 450 °C, indicating that GeO was volatilized during GeO_2 formation and deposited on to the SiO_2 surface as GeO_2 . In contrast, there are no peaks but small signals which look like Ge oxide in the expanded spectrum shown in the inset of Fig. 2(b) obtained from the sample oxidized at 400 °C, which suggests that GeO desorption rate is quite slow at 400 °C.

The surface conditions of the GeO_2 films formed at various temperatures were measured using an AFM. The AFM results [Figs. 3(a) and 3(b)] show that a relatively smooth surface is formed at 400 °C, while the rms roughness increases with the oxidation temperatures above 400 °C. This indicates that GeO volatilized during thermal oxidation above 400 °C which is agreement with the XPS results (see Fig. 2).

C-V characteristics of Al/ GeO_2 /p-Ge capacitors with and without GeO desorption were evaluated. GeO_2 films ($\sim 10 \text{ nm}$) were formed by thermal oxidation of Ge substrates between 400 and 550 °C. The results are shown in Fig. 4. The C-V curves of samples oxidized above 450 °C show a large V_{FB} shift and C-V hysteresis. Moreover, neither improvements nor deteriorations were observed between the characteristics of samples oxidized above 450 °C. By using Ge oxidation at 400 °C, on the other hand, the C-V hysteresis and the V_{FB} shift was recovered toward the ideal value compared to the samples oxidized at higher temperatures. These results prove that interface formation between GeO_2/Ge at low temperature is effective to improve the electrical properties due to a quite slow desorption rate of GeO.

However, a relatively large V_{FB} shift of $\sim 1.4 \text{ V}$ still remained in the curve compared to an ideal one, as shown in Fig. 4. Furthermore, there were almost no changes of frequency distribution in the C-V curves which usually caused by the minority carrier generation via the interface states at GeO_2/Ge . This suggests that the density of interface states (D_{it}) is independent of oxidation temperature between 400 and 550 °C, or that other defects, such as subgap states in GeO_2 bulk formed by GeO desorption,¹² dominate the minority carrier response.

B. Metal/ GeO_2 interface and GeO_2 bulk

To improve the frequency distribution and the remaining V_{FB} shift in the Al/ GeO_2 /Ge capacitors, postmetallization annealing (PMA) was carried out in this work at 300 °C in N_2 ambient. Measured C-V curves of the Al/ GeO_2 /Ge capacitors oxidized at 400 °C with and without the PMA are shown in Fig. 5. The V_{FB} values of all specimens estimated by fitting with an ideal curve are described in Table I. As shown in the figure and the table, the V_{FB} shifts were drastically improved by using PMA. Although the slope of the C-V curve is less steep than that of an ideal curve, there were no V_{FB} shifts at all in the C-V curve of samples oxidized at 400 °C with PMA. Improvements of frequency distribution were also observed in C-V curves of samples treated with PMA. Here, please note that the improvements of these V_{FB} shift and minority carrier generation were observed not only

FIG. 3. (Color online) (a) AFM images ($1 \times 1 \mu\text{m}^2$) of surface of GeO₂ (~ 10 nm) thermally oxidized at several temperatures. (b) rms roughness of the GeO₂ films formed at 400–600 °C. Although the results show a flat surface formed at 400 °C, the roughness increased above 450 °C due to GeO desorption during the oxidation.

in the Al/GeO₂/Ge capacitors, but in Al/SiO₂/Si systems as well. Figure 6 shows that C-V characteristics of the Al/SiO₂(15 nm)/p-Si capacitor fabricated by a thermal oxidation of p-type Si (100) at 1000 °C with and without PMA at 300 °C in N₂ ambient. The frequency dependence and the V_{FB} shift, existing in the as-oxidized curve, are fully eliminated after PMA. These PMA effects on the Al/SiO₂/Si structure are consistent with those on Al/GeO₂/Ge structures. It is known that silicon monoxide (SiO) desorbs during annealing of SiO₂/Si above 800 °C,^{13,14}

Hence, it was concluded that the mechanism of the improvements of electrical properties in Al/GeO₂/Ge capacitors is same as that of Al/SiO₂/Si capacitors.

To explain the mechanism of improvements of those electrical properties we focused on the increase in the accumulated capacitance after PMA as shown in Fig. 5. The CET values of Al/GeO₂/Ge capacitors fabricated with and without PMA at 300 °C in N₂ were examined for various GeO₂

thicknesses. Figure 7 compares CET values before and after PMA. After PMA, the CET values were as much as ~ 1.8 nm smaller, which is independent of the initial GeO₂ thickness. These results clearly show that GeO₂ films either became thinner, or either aluminum oxide or germanium aluminate layer, which has a higher κ -value than GeO₂, was formed at the top interface between the Al electrode and the GeO₂ layer during PMA. Considering that the V_{FB} shifts were also recovered by PMA when using other electrode metals such as Au (not shown), which do not form a stable oxide, the former should be the prominent factor of the V_{FB} improvement.

To demonstrate the mechanism of GeO₂ reduction and to clarify the role of the metal layer in improvements of the electrical characteristics, GeO desorption during low temperature annealing of metal/GeO₂/Ge structures were investigated using TDS. First, Al and Au films were deposited on thermally oxidized GeO₂/Ge. In addition, each metal/GeO₂/Ge structure was annealed in a TDS chamber. The TDS spectra of GeO desorbed from these stacks are shown in Fig. 8 as triangular symbols in red and blue, respectively. The data of GeO₂/Ge without metal deposition is also shown as a reference (gray triangles). Although there were no signals of GeO detected around 300 °C from GeO₂/Ge stacks, GeO signals were clearly observed for the metal/GeO₂/Ge structures at that temperature. At temperatures above 400 °C, GeO desorbed from all specimens indi-

FIG. 4. C-V characteristics of Al/GeO₂/p-Ge capacitors fabricated at various oxidation temperatures measured at 1, 10, 100, and 1000 kHz. Oxidation at 400 °C is effective to improve the negative V_{FB} shift and the C-V hysteresis.

FIG. 5. C-V characteristics of Al/GeO₂/p-Ge capacitors fabricated by thermal oxidation at 400 with and without PMA at 300 °C. Drastic improvements of V_{FB} shift and the minority carrier generation were achieved by using PMA.

TABLE I. The oxidation temperature and amount of flat-band voltage shift (ΔV_{FB}) of each samples of Al/GeO₂/Ge capacitors estimated from C-V curves fitted with an ideal curve.

Sample	Oxidation temperature (°C)	V_{FB} (V)
As-oxidized	400	1.4
As-oxidized	450	2.0
As-oxidized	500	2.0
As-oxidized	550	2.0
w/PMA	400	0.0

cating that they desorbed from the GeO₂/Ge interface. To determine the mechanism of initial GeO desorption at 300 °C, GeO₂ films were deposited on thermally oxidized SiO₂/Si. Then, metal (Al or Au)/GeO₂/SiO₂/Si and a reference sample of GeO₂/SiO₂/Si were annealed in a TDS chamber, as illustrated in the inset of Fig. 8. The results of GeO desorption from these samples are shown in Fig. 8 as circular symbols. The fact that no peaks were detected for GeO₂/SiO₂/Si suggests that the GeO desorption present in metal/GeO₂/Ge stacks at high temperatures originates from the interface between GeO₂ and Ge. Meanwhile, after metal films were deposited on GeO₂, GeO signals were only observed at low temperatures indicating that GeO desorbed from the interface of metal/GeO₂ at around 300 °C. Moreover, those additional GeO signals were observed not only from the Al/GeO₂, but also from the Au/GeO₂ interface. Note that there is a possibility that these GeO desorbs not through the metal layer but from the edge of the metal film. Recently, it has been reported that GeO desorbs from a solid GeO [GeO(s)] layer at >300 °C.¹⁵ In our case, the metal could be a catalyst for the formation of GeO(s) which then desorbs as GeO gas,¹⁶

Judging from these TDS analysis, GeO was volatilized by an interdiffusion process between the metal and the GeO₂ film at around 300 °C. A structural change at the top interface caused by the metal catalyzed GeO desorption leads to the

FIG. 6. (Color online) Measured C-V characteristics of Al/SiO₂(15 nm)/p-Si structures fabricated by a thermal oxidation of Si substrate at 1000 °C with and without PMA at 300 °C in N₂.

FIG. 7. CET values of Al/GeO₂/Ge capacitors before PMA vs their CET value after PMA. After PMA, CETs were reduced by ~1.8 nm which is independent of initial GeO₂ thickness. These results suggest that the GeO₂ layer became thinner after the PMA.

improvement of the electrical properties. It sounds reasonable that the origin of the negative V_{FB} shift such as Fermi level pinning should be the top interface. Considering from that the minority carrier generation was suppressed by PMA, however, the interface condition of GeO₂/Ge must be improved. Hence, there is a strong possibility that the improvements of GeO₂/Ge interface attribute to the structural change at the metal/GeO₂ interface. During PMA, for example, oxygen or its vacancies which created at the top interface by the GeO desorption might diffuse to the bottom interface.

IV. SUMMARY

In this paper, the relationship between GeO desorption and the electrical characteristics of metal/GeO₂/Ge capacitors, fabricated by thermal oxidation of Ge substrates, was investigated. For these metal/GeO₂/Ge stacks, two processes

FIG. 8. (Color online) TDS signals of GeO desorbed from metal/GeO₂/Ge and metal/GeO₂/SiO₂/Si structures, respectively. GeO spectra without metal cap layer are also shown as references. There are additional GeO signals desorbed from the specimens with a metal cap layer around 300 °C. These results clearly show that the GeO desorbed from the metal/GeO₂ interface. The inset shows a model of those TDS analysis results.

of GeO desorption at different sites and at different temperatures were observed by TDS measurements. During the oxidation of Ge at temperatures above 400 °C, GeO desorbs from the GeO₂/Ge interface, which leads to a deterioration of the electrical properties. On the other hand, those deteriorated electrical properties were significantly improved by PMA at 300 °C in N₂ due to a structural change caused by metal catalyzed GeO desorption.

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