Extended Abstracts of the 2006 International Conference on Solid State Devices and Materials, Yokohama, 2006, pp. 442-443

P-1-21

Composition Dependence of Work Function in Metal (Ni, Pt)-Germanide Gate Electrodes

Daisuke Ikeno[1], Kouhei Furumai[1], Hiroki Kondo[1†], Mitsuo Sakashita[1], Akira Sakai[1], Masaki Ogawa[2], and Shigeaki Zaima[1]

[1]Nagoya University, Graduate School of Engineering, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Phone: +81-52-789-3819 †E-mail: hkondo@alice.xtal.nagoya-u.ac.jp

[2]Nagoya University, Center for Cooperative Research in Advanced Science & Technology, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

1. Introduction

As metal-oxide-semiconductor (MOS) devices are scaled down to 45 nm node, metal gate electrodes are required to avoid poly-Si depletion and dopant penetration problems. Metal-germanide is one of promising candidates, because it can be formed by conventional ULSI processes and equipments. The low resistivity and tunable work function are also desirable. In this study, electrical (work function and resistivities) and structural properties of metal (Ni, Pt)-germanide MOS gate electrodes with various metal-germanium composition ratios were systematically evaluated. The composition ratio dependence of work function was discussed based on the electronegativity.

2. Experimental

MOS capacitors which have metal (Ni, Pt)-germanide gate electrodes with various metal-Ge composition ratios were fabricated. A p-type Si (100) wafer was used as a substrate. After diluted-HF treatment, gate SiO_2 films (12-35 nm) were grown by thermal oxidation. Ge (19.0-43.7 nm) and Ni (27.0-35.3 nm) or Pt (14.8-39.0 nm) were sequentially deposited on the SiO_2 by electron beam evaporation at room temperature. Each film thickness was determined from the atomic density ratio of required germanide phases. Ni/Ge/SiO_2/Si and Pt/Ge/SiO_2/Si samples were then subjected to rapid thermal annealing (RTA) at 500°C and 600°C, respectively, for 30 sec in N_2 atmosphere for germanidation. Finally, the MOS capacitors were annealed at 350-400°C for 30-60 min in H_2 atmosphere.

3. Results and Discussion

Figures 1(a) and (b) are X-ray diffraction profiles of Ni/Ge/SiO_2/Si and Pt/Ge/SiO_2/Si samples after RTA, respectively. Diffraction peaks observed in each profile come from almost the single crystalline phase, which indicates that the MOS capacitor predominantly consists of single-phase germanide electrode. Furthermore, it is found that various types of Ni-germanide (Ni-Ge) and Pt-germanide (Pt-Ge) phases are successfully formed by changing the thickness ratio of metal to Ge.

Figures 2(a) and (b) show cross-sectional TEM images of Ni_5Ge_3 and $PtGe_2$, respectively. Unreacted Ge layers are not found at both interfaces of Ni_5Ge_3/SiO_2 and $PtGe_2$/SiO_2. Therefore, germanidation proceeded completely to the interfaces of Ni_5Ge_3/SiO_2 and $PtGe_2$/SiO_2. It can be clearly seen that both Ni_5Ge_3 and $PtGe_2$ have columnar grain structures and similar grain structures were also observed in Ni-Ge and Pt-Ge with other metal-Ge composition ratios.

Figure 3 shows composition ratio dependence of resistivities of metal-germanide films. Most of the Ni-Ge and Pt-Ge have lower resistivities than that of a conventional poly-Si gate (~1000 μΩ·cm) [1]. Only a $PtGe_3$ has a much higher resistivity compared to other germanides. The resistivity of Ni-Ge slightly increases with increasing the content of Ni.

High- and low-frequency capacitance-voltage (C-V) characteristics of a MOS capacitor with a Ni_5Ge_3 gate electrode are shown in Fig. 4. The capacitance in the inversion region (C_{inv}) is almost identical with that in the accumulation region (C_{acc}). Interface state densities (D_{it}), estimated from the difference between high- and low- frequency capacitances at a midgap voltage, were about 3×10^{-11} $cm^{-2}eV^{-1}$. For all capacitors fabricated in this study, gate depletion did not arise and D_{it} is negligible. This allows us to obtain work function values of gate electrodes from the capacitance equivalent thickness (CET) dependence of the flat-band voltage obtained from the high frequency C-V curve. Figure 5 shows the CET dependence of flat-band voltages for the MOS capacitors with the Ni-Ge and Pt-Ge gate electrodes. The work function values of their gate electrodes can be estimated from the y-intercepts of lines in Fig. 5.

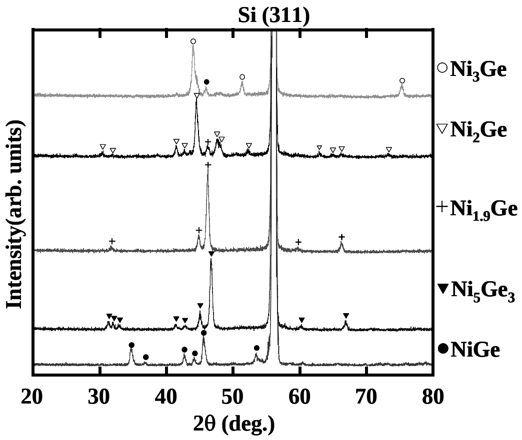
Figure 6 shows Ni and Pt composition dependence of the work function for the Ni-Ge, Pt-Ge gate electrodes. Reported values of the nickel-silicide (Ni-Si) case are also plotted for comparison [2]. The work function of Ni-Ge is found to decrease with increasing Ni content, while that of Ni-Si increases. On the other hand, the work function of Pt-Ge increases with increasing Pt content. Here, we have tried to explain this composition dependence of work function by considering electronegativity of each metal-germanide. The electronegativities of Ni-Ge, Ni-Si and Pt-Ge were approximated from geometric means of Pauling electronegativities of Ni, Pt, Ge and Si [3-5]. Figure 7 shows the work function values of Ni-Ge, Ni-Si and Pt-Ge depending on their electronegativities. While it is well known that the work function of pure metals and metal alloys has a tendency to increase with the electronegativity [6], it is found in this study that metal-silicide and metal-germanide have a similar tendency. This result indicates that electronegativity gives an indication of work function of metal-group IV semiconductor compounds.

4. Conclusions

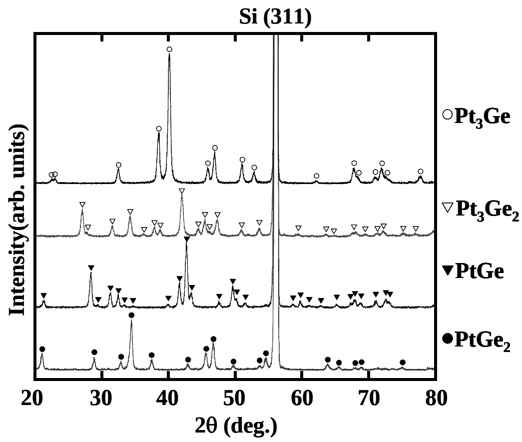
We investigated composition ratio dependence of electrical and structural properties in metal-germanide gate electrode systems. Various types of Ni-Ge and Pt-Ge phases were successfully formed by changing thickness ratio of Ni and Pt to Ge, respectively. The work function of Ni-Ge decreased with increasing Ni content, while that of Pt-Ge increased with increasing Pt content. Therefore, the work function of Ni-Ge and Pt-Ge can be controlled by modulating composition ratio. The systematic analysis revealed the work function of Ni-Ge, Pt-Ge and Ni-Si critically depends on their electronegativities.

References

[1] T. Makino *et al*., Solid-St. Electron. **24**, (1981) 49.
[2] J. A. Kittl *et al*., VLSI Tech. Proc., (2005), p. 72.
[3] Robert G. Parr *et al*., J. Am. Chem. Soc. **104**, (1982) 3801.
[4] L. Pauling, J. Am. Chem. Soc. **54**, (1932) 3570.
[5] A. L. Allred, J. Inorg. Nucl. Chem. **17**, (1961) 215.
[6] W. Gordy *et al*., J. Chem. Phys. **24**, (1956) 439.

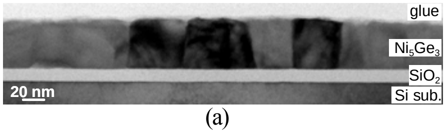


(a)

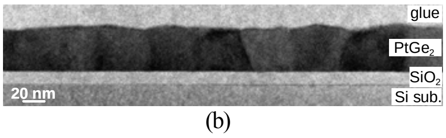


(b)

Fig. 1 XRD profiles of (a) Ni/Ge/SiO_2/Si and (b) Pt/Ge/SiO_2/Si samples after RTA.



(a)



(b)

Fig. 2 Cross-sectional TEM images of (a) Ni_5Ge_3 and (b) $PtGe_2$ films.

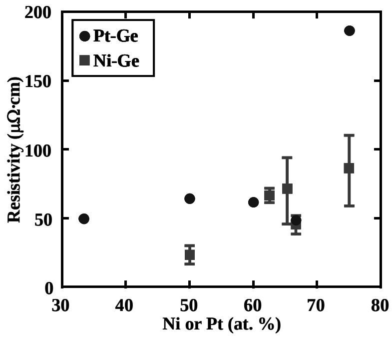


Fig. 3 The metal composition ratio dependence of the resistivities for the Ni-Ge and Pt-Ge films.

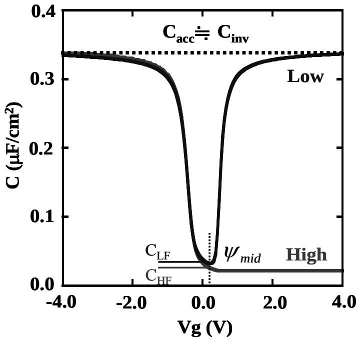


Fig. 4 The low- and high-frequency C-V characteristics of the MOS capacitor with the Ni_5Ge_3 gate electrode.

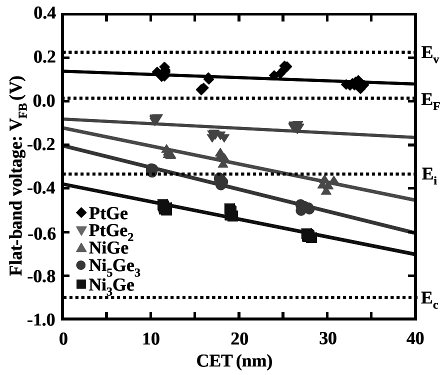


Fig. 5 CET dependence of the flat-band voltages for the MOS capacitors with the NiGe, Ni_5Ge_3, Ni_3Ge, $PtGe_2$ and PtGe gate electrodes.

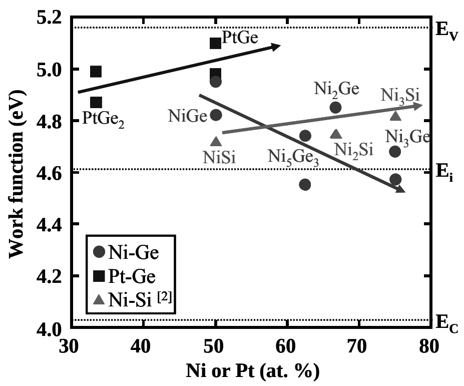


Fig. 6 The metal (Ni, Pt) composition ratio dependence of the work function values for the Ni-Ge, Ni-Si[2] and Pt-Ge gate electrodes.

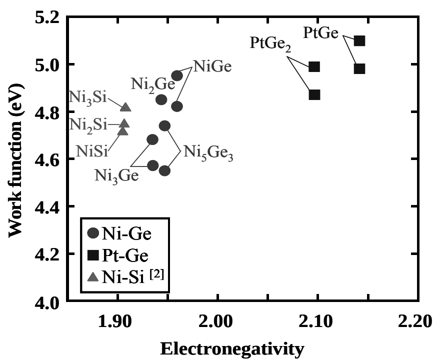


Fig. 7 The dependence of the work function values on the electronegativities for the Ni-Ge, Ni-Si[2] and Pt-Ge gate electrodes.