Multilayer TiNi Alloys as Gate Metal for InGaAs MOS devices

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Abstract

The multilayer TiNi alloys have been successfully applied as the gate metals for HfO₂/In₀.₅₃Ga₀.₄₇As MOS devices in this study. The EWF of TiNi alloys was found to increase from 4.41 eV for as-deposited sample to 4.62 eV after the alloy was annealed due to the diffusion of Ni atoms into Ti layer. The multilayer TiNi alloy remained amorphous-phase with small WFV until annealed at 600 °C. The TiNi alloy is thermally more stable as compared to either Ti or Ni metal because the TiO₂/Ni interfacial layer prevents the diffusion of Ni atoms into HfO₂ film and the further reaction of Ni atoms into Ti layer. The multilayer TiNi alloy remained amorphous-phase with small WFV until annealed at 600 °C. The TiNi alloy is thermally more stable as compared to either Ti or Ni metal because the TiO₂/Ni interfacial layer prevents the diffusion of Ni atoms into HfO₂ film and the further reaction of Ni atoms into Ti layer.

1. Introduction

Metal gate on high-k dielectrics is currently an important issue needed to be solved for III-V MOS devices. The low work function (WF) metals such as Ti, Al, and Ta react easily with O in metal/oxide interface while the high WF metals such as Ni and Pt diffuse easily into the oxide layer. The binary alloys of low WF metals and high WF metals were adopted on oxide/Si substrate to overcome the above problems. However, the results cannot be directly applied to HfO₂/InGaAs structure as controlling samples. The amorphous metal used as gate material provides a small threshold voltage variation compared to either Ti or Ni metal because the TiO₂/Ni interfacial layer prevents the diffusion of Ni atoms into HfO₂ film and the further reaction of Ni atoms into Ti layer.

2. Experimental

The epitaxial wafers used in this study consisted of 100 nm InGaAs layer on n⁺-InP substrate (5×10¹⁷/cm³ Si-doped n-type wafer) grown by solid source molecular beam method. 3 samples with different HfO₂ thicknesses were prepared (7.76 nm, 11.64 nm, and 15.52 nm). The samples were annealed in forming gas (FG) at 450 °C for 5 minutes by rapid thermal annealing (RTA) after oxide deposition. The multilayer TiNi alloys of 38 at. %, 52 at. %, and 80 at. % Ti (namely S₁, S₂, and S₃, respectively) were deposited on HfO₂/InGaAs using alternate deposition of 5 Ti layers and 5 Ni layers by E-gun evaporation.

\[ Ti \text{ at. \%} = \frac{1}{1 + 1.61 \times \frac{H_{Ni}}{H_{Ti}}} \times 100\% . \] (1)

50 nm Ni (sample CS₁) and 50 nm Ti (sample CS₂) were also deposited as gate metals for HfO₂/InGaAs MOS structure as controlling samples.

3. Result and discussion

![Fig. 1(a)](image)

Fig. 1(a) The flat band voltage versus HfO₂ thicknesses used to extract EWF of the samples S₁, S₂, and S₃ as deposited, annealed at 350°C for 30s in FG, and further annealed at 400°C for 5 minutes in FG; (b) the EWF of TiNi alloys versus atomic percentage of Ti, the Ti EWF was extracted from as deposited sample: (c) J-V curves of samples CS₁, CS₂, S₁, S₂, and S₃ with 7.76 nm HfO₂ after annealing at 350°C for 30s in FG, respectively; (d) J-V curves of samples CS₁, and S₃ with 7.76 nm HfO₂ after further annealing at 400°C for 5 minutes in FG.

Fig. 1(a) shows the flat band voltages of samples S₁, S₂, and S₃ versus HfO₂ thickness. The intercept of V_{FB} of samples S₁, S₂ and S₃ shifted ~ 0.21 V (from ~ 0.11 V to ~ 0.10 V) after annealing. This phenomenon was not observed for sample CS₁ (data not shown). The EWF of sample CS₁ was reported to be 5.55 eV in our previous study [2]. The changes in V_{FB} intercept of samples S₁, S₂, and S₃ after annealing are due to the diffusion of Ni atoms into Ti layer. Fig. 1(b) shows the EWF of alloys versus atomic percent-
age of Ti. Note that the EWF of sample CS$_2$ in Fig. 1(b) is extracted from as deposited sample because the tremendous reaction of Ti with HfO$_2$ layer leads to the breakdown of CS$_2$ MOSCAP after annealing shown in Fig. 1(c). The EWF of the annealed alloy was found to be around 4.62 eV which is close to the conduction band of InGaAs. The results indicate that first Ti layer contacting the HfO$_2$ layer determines the EWF of the alloy. The samples CS$_1$ and S$_2$ were further annealed at 400°C in FG for 5 minutes by RTA. The leakage current of the sample CS$_1$ was found to increase to $\sim 10^{-8}$ A/cm$^2$ at $V_{FB} + 1$ (V) while that of sample S$_2$ remained at $\sim 10^{-9}$ A/cm$^2$ as shown in Fig. 1(d). The stability of TiNi/HfO$_2$ interface (due to the formation of the TiO$_x$Ni interfacial layer) prevents the additional diffusion of Ni atoms into HfO$_2$ film and keeps the gate leakage current of sample S$_2$ unchanged.

**Fig. 2 XPS spectra of (a) Ti 2p peaks of Ti/HfO$_2$ and TiNi/HfO$_2$ interfaces of samples CS$_1$ and S$_2$ as deposited and after annealing, (b) Ni 2p$_{3/2}$ peaks of Ni/HfO$_2$ and TiNi/HfO$_2$ interfaces of samples CS$_1$ and S$_2$ as deposited and after annealing, (c) Hf 4f peaks of Ni/HfO$_2$ interface of samples CS$_1$ and the clean HfO$_2$ surface after annealing, respectively.**

The Ti 2p$_{3/2}$ peak of sample S$_2$ shifted 0.28 eV after annealing. These shifts are comparable to that of $V_{FB}$ intercept shown in Fig. 1(a). The binding energy of Ni 2p$_{3/2}$ peak of sample CS$_1$ remained unchanged after annealing as shown in Fig. 2(b) and the Hf 4f$_{7/2}$ peak positions of samples CS$_1$ and clean HfO$_2$ surface are kept the same as shown in Fig. 2(c), indicating that the shift of $V_{FB}$ intercept shown in Fig. 1(a) is due to the diffusion of Ni atoms into Ti layer rather than the gate-metal/oxide reaction. The In–O bond was observed in sample S$_2$ and the Ni/HfO$_2$ interface after annealing shown in Fig. 2(a) and (c), respectively.

Fig. 3 shows the grazing angle X-ray diffraction (GXRD) spectra of sample S$_2$. The as-deposited sample reveals no crystalline peak, suggesting that the as-deposited alloy has nano-crystalline structure. The sample was annealed at 300°C to 800°C for 30s in FG. The crystalline peak is not found until annealed at 600°C, indicating that the alloy has amorphous phase due to the inter-diffusion of Ni and Ti. Literature reported that the amorphous phase or nano-crystalline structure of metal alloy induces a small EWF variation [1]. The results demonstrate that the EWF variation of TiNi alloy is still small until annealed at 600°C. The inset of Fig. 3 shows the GXRD spectra of sample S$_2$ after annealing at 350°C for 30s in FG and further annealing at 400°C for 5 minutes in FG. After further annealing, the sample S$_2$ is found to remain the amorphous-phase which has a small EWF variation.

**Fig. 3 The GXRD for as deposited and annealed multilayer TiNi alloy; inset: the Grazing XRD for sample S$_2$ after annealing at 350°C for 30s and further annealing at 400°C for 5 min. in FG.**

### 3. Conclusion

In conclusion, the properties of TiNi alloys have been studied for In$_{0.53}$Ga$_{0.47}$As NMOS devices. It is found that the EWF of the TiNi alloys increased from ~ 4.41 eV in as-deposited sample to ~ 4.62 eV after annealing. The multilayer TiNi alloy exhibited amorphous-phase which has small work function variation until annealed at 600°C.

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