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Dopant effects on the thermal stability of FUSI NiSi

P. Zhao, M.J. Kim, B.E. Gnade, R.M. Wallace *

Materials Science and Engineering, University of Texas at Dallas, Richardson, TX 75083, USA

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Abstract

The thermal stability of fully silicided (FUSI) NiSi with arsenic or boron doping on silicon on insulator (SOI) was investigated. After the stacks were subjected to a typical back-end of line (BEOL) thermal annealing in a N_2 ambient, abnormal oxidation of As doped FUSI NiSi stacks is observed by X-ray photoelectron spectroscopy (XPS), and confirmed by high-resolution transmission electron microscopy (HRTEM). X-ray diffraction (XRD) results show Ni-rich phases like Ni_3Si are formed due to abnormal oxidation of FUSI NiSi. In contrast to As doped stacks, no phase transformation nor abnormal oxidation are observed for B doped stacks under similar annealing. However, backside secondary ion mass spectrometry (SIMS) results indicate B penetration through a 3 nm SiON layer into the Si channel after N_2 annealing for 4 h at 400 °C. There is no evidence for Ni diffusion into the Si channel for B doped stacks. However, Ni penetration into the Si channel is observed for As doped stacks due to the enhancement of abnormal oxidation of FUSI NiSi.

Keywords: FUSI; NiSi; Work function; CMOS; Metal gate; Thermal stability

1. Introduction

FUSI NiSi metal gates have received significant attention recently, and appear to be a promising metal gate for replacing the conventional poly-Si gate due to the low resistivity, scalability, and work function tunability by pre-doping poly-Si with the proper dopants [1–3]. The work function tuning range of FUSI NiSi gates by pre-doping poly-Si or amorphous Si spans most of the Si band gap depending on dopants and dose. It has been reported by Kedzierski et al. that the work function of NiSi can be controlled over a range of 0.4 eV by doping with boron or arsenic, and the observed implantation dose for saturation of the work function is greater than 1 to 3×10^{15} cm^{-2} [4,5]. However, there remain many challenges for the successful integration of FUSI NiSi metal gates. The thermal stability of NiSi is strongly dependent on the dopants when high temperature post-silicidation furnace annealing or back-end of line (BEOL) thermal treatment is applied due to the oxidation of NiSi, and especially for As-doped stacks [6]. Recently, it was reported that the work function of FUSI Ni silicide gates also strongly depends on Ni silicide phases. Ni rich silicides (Ni_3Si, N_2Si) with the same work function (~4.8 eV) on SiON or HfSiON were used for PMOS gates, and a low $V_t = -0.33$ V was obtained for these devices [7–9]. Therefore, the phase stability of FUSI NiSi due to dopant effects is one of the important questions to be answered once FUSI NiSi metal gates are exposed to a BEOL thermal processing.

The work function of FUSI NiSi metal gates is tuned by dopant pileup at the interface of FUSI NiSi/dielectric during silicidation. However, there is a possibility that dopants piled up at the interface, as well as weakly bonded Ni, could penetrate into the Si channel upon annealing. The high diffusivity of elemental Ni in Si is close to that of hydrogen [10]. It has been reported that Ni diffusion is faster in bulk silicon than on the Si surface [11]. It has also been reported that deep level defects in Si detected by DLTS for a Ni/Si sample annealed at 400 °C are related to Ni atom diffusion [12]. Ni diffusion from Ni films through 0.5–5 nm SiO_2 into the underlying Si channel at annealing temperatures $T \geqslant$ 427–477 °C has been reported and is dependent upon SiO_2 thickness [13,14].

* Corresponding author. Tel.: +1 972 883 6638; fax: +1 972 883 5725.
E-mail address: rmwallace@utdallas.edu (R.M. Wallace).

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Recently, we have reported Ni diffusion from FUSI NiSi metal gates without doping into the Si channel upon exposure to a typical BEOL thermal budget [15,16]. Ni may also penetrate into the Si channel due to the phase instability of FUSI NiSi metal gates resulting from dopant effects. It has been recently reported that dopants segregate from FUSI NiSi into gate dielectrics such as SiO_2 and HfSiON, resulting in an EOT increase and work function modulation [17]. The interdiffusion of impurities into the Si channel originating from the gate electrode through thin gate dielectric layers may be expected to degrade the device performance such as reliability, mobility and gate leakage current [18–20].

In this paper, we study dopant effects on the thermal stability of FUSI NiSi metal gates on a silicon-on-insulator (SOI) substrate after exposure to a typical BEOL thermal process. The phase stability and oxidation of doped FUSI NiSi, and impurity (B, As, Ni) diffusion behavior are discussed in detail.

2. Experiments

FUSI NiSi metal gates on SOI substrates were used for thermal stability studies. Thin body SOI structures (17 nm TiN/46 nm Ni/64 nm poly-Si/3 nm SiON/55 nm Si/140 nm SiO_2/Si), FUSI NiSi metal gates were formed by one step rapid thermal annealing (RTA) in flowing N_2 at 450 °C for 1 min. After silicidation and removal of TiN and the unreacted Ni, the stack structures (90 nm FUSI NiSi/3 nm SiON/55 nm Si/140 nm SiO_2/Si) were annealed in a high purity N_2 ambient in a tube furnace. Consistent with a contemporary BEOL process, the typical annealing temperature is 400 °C. Since the duration of the BEOL anneal is on the order of minutes for thermal treatments of the layers associated with etch-stop, low-κ dielectric deposition and Cu surface cleaning, the total time for multiple layers of metallization could add up to 90–120 min, or even more. In this study, long duration anneals (up to 4 h) were conducted to search for evidence of dopant and Ni diffusion.

The phase stability and oxidation of FUSI NiSi metal gates were examined by grazing incident X-ray diffraction (GIXRD) and X-ray photoelectron spectroscopy (XPS), respectively. High-resolution transmission electron microscopy (HRTEM) was performed to study the microstructure of FUSI NiSi metal gates before and after post-silicidation annealing. A 4-point probe measurement was used to determine sheet resistance of FUSI NiSi metal gates.

The outdiffusion of Ni and dopants from FUSI NiSi metal gates through the 3 nm SiON layer into the Si channel after N_2 annealing was studied by *backside* secondary ion mass spectrometry (SIMS) profiling methods to avoid ion beam mixing (''knock-on'') artifacts typically seen in conventional front-side dynamic SIMS analysis [21,22]. The backside SIMS sample preparation was performed before the stacks were subjected to backside SIMS analysis. The sample preparation procedure is as follows: the Si substrate is polished down to less than 50 μm thickness and scratch free by inspection. The remaining Si was removed in a solution of tetramethyl-ammonium hydroxide solution at 80 °C. Finally, the buried oxide (SiO_2) was removed with 5% HF. The final stack structures are: 17 nm TiN/46 nm Ni/64 nm poly-Si/3 nm SiON/55 nm Si (as-received) or 90 nm Ni silicide/3 nm SiON/55 nm Si (after silicidation or post-silicidation annealing).

The final stacks were subjected to backside SIMS analysis [23]. A magnetic sector SIMS instrument was used with 3.0–8.0 keV O_2^+ ions at 38 ° incidence to obtain B, As and Ni depth profiles. High mass resolution conditions were utilized to separate ^{58}Ni from $^{28}Si + {}^{30}Si$ and $^{29}Si_2$ molecular ion interferences, which occur at the same nominal mass. Several profiles were acquired to determine reproducibility. Ni concentrations were calibrated with Ni implants in Si.

3. Results and discussion

3.1. Thermal stability

Fig. 1 shows XPS results for FUSI NiSi metal gates with As doping after various anneals. The Si2p feature at ~103.5 eV and the O1s peak at ~533.0 eV for fully silicided films (formed at 450 °C for 1 min), which are assigned to Si–O bonds, vanish after the *in situ* removal of ~6 nm by Ar^+ sputtering (''surface cleaning''). This indicates that the oxidation is located at the surface of FUSI NiSi films (Fig. 1a and b). After FUSI NiSi films were subjected to post-silicidation N_2 annealing for 30 min or longer at 400 °C, it is observed that the peak intensities of Si2p and O1s both assigned to Si–O bonds are almost the same before and after Ar^+ sputtering for 20 min or even longer, suggesting that the oxidation is not just located at the surface. The O/Si ratio is close to 2/1, indicating that a SiO_2 layer is formed. The intensity of Ni2p peaks assigned to Ni–Si bonds (~853.0 eV) [24] formed at 450 °C for 1 min annealing decreases with post-silicidation annealing time, and is below the XPS detection limit after 4 h annealing at 400 °C. As shown in Fig. 1a–c, the data also suggests that the SiO_2 thickness after post-silicidation annealing is >10 nm based on the escape depth of photoelectrons. We speculate that the source of O_2 is associated with the purged furnace tube employed for the anneals. This abnormal oxidation of FUSI NiSi films is in good agreement with previous reports [25]. We note that a shift of both the Si2p and O1s features after Ar sputtering by ~1 eV is observed and is attributed to a differential charging effect associated with the removal of the surface region by the Ar ions. In Fig. 1d, the Arsenic concentration for the FUSI NiSi films formed at 450 °C for 1 min after surface Ar^+ sputtering is ~15 at.% which indicates As out-diffusion to the FUSI NiSi surface. After post-silicidation N_2 annealing and surface Ar^+ sputtering, the As concentration on the surface falls to ~2.3 at.% determined by XPS, indicating As outdiffusion.

In contrast to As doped stacks, B doped FUSI NiSi films show much better stability. Fig. 2 shows the Si2p and O1s spectra for boron doped FUSI NiSi films with var-