Silicidation of Ni(Yb) Film on Si(001)

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The influence of the addition of Yb to Ni on the silicidation of Ni was investigated. The Ni(Yb) film was deposited on a Si(001) substrate by co-sputtering, and silicidation was performed by rapid thermal annealing (RTA). After silicidation, the sheet resistance of the silicide film was measured by the four-point probe method. X-ray diffraction and micro-Raman spectroscopy were employed to identify the silicide phases, and the redistribution of Yb after RTA was characterized by Rutherford backscattering spectrometry and Auger electron spectroscopy. The influence of the Yb addition on the Schottky barrier height (SBH) of the silicide/Si diode was examined by current–voltage measurements. The experimental results reveal that the addition of Yb can suppress the formation of the high-resistivity Ni₂Si phase, but the formation of low-resistivity NiSi phase is not affected. Furthermore, after silicidation, most of the Yb atoms accumulate in the surface layer and only a small number of Yb atoms pile up at the silicide/Si(001) interface. It is believed that the accumulation of a small amount of Yb at the silicide/Si(001) interface results in the SBH reduction observed in the Ni(Yb)Si/Si diode.

Key words: Ytterbium addition, nickel silicidation, Schottky barrier height

INTRODUCTION

The self-aligned silicide (SALICIDE) process has been used extensively in complementary metal-oxide semiconductor (CMOS) integrated circuits to reduce the source/drain contact resistance and conduction resistance.^{1–3} As an alternative to TiSi₂ and CoSi₂, nickel monosilicide (NiSi) has been used in high-performance CMOS devices and has attracted growing attention in sub-45-nm CMOS devices.^{4–8} However, the contact resistance of NiSi on *n*-type Si (for NMOS) is high due to the high Schottky barrier height (SBH) of NiSi (~0.65 eV). On account of the limited dopant solubility in Si, reduction of the SBH is a more effective way to reduce the source/drain contact resistance.

Ytterbium (Yb) is known to have a low work function (WF) of ~2.59 eV, and a low SBH of

~0.27 eV has also been reported for Yb silicide.⁹ As a possible extension of the NiSi technology, Yb silicide has been proposed as the low-SBH source/drain contact in NMOS devices.^{9–11} However, there are still serious problems such as oxidation and pinhole formation during Yb silicidation. In the work reported here, an alternative way to lower the SBH of NiSi on *n*-type Si is demonstrated by silicidation of the Ni film doped with Yb.

EXPERIMENTAL DETAILS

After standard RCA cleaning with a final dip in diluted HF, *n*- and *p*-type Si (001) wafers with a resistivity of 4 to 8 Ω cm were immediately loaded into a BALZERS physical vapor deposition (PVD) system with a base pressure less than 2×10^{-5} Pa. A 22-nm-thick Ni (Yb) film was deposited on the Si substrate using a co-sputtering process at a working pressure of 5×10^{-1} Pa. The composition of the Ni(Yb) film was controlled by adjusting the individual sputtering power applied to the Ni and Yb

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targets. After deposition, rapid thermal annealing (RTA) was carried out under high-purity argon at temperatures from 300°C to 900°C for 60 s. After RTA, in order to perform the electrical measurements, a selective etching process was applied to the diode samples so that only the silicide was retained. Afterwards, backside ohmic contacts were fabricated by sputter deposition of aluminum to prepare the diode samples. The diameter of the Ni(Yb) dot on the front side of the diode was 600 μm . The sheet resistance was measured by the four-point probe (FPP) method, and X-ray diffraction (XRD) was used to identify the phases of the films. Micro-Raman spectroscopy (MRS) was also used to determine the NiSi phases. Rutherford backscattering spectrometry (RBS) and Auger electron spectroscopy (AES) were employed to investigate Yb redistribution. The current-voltage (I - V) characteristics of the NiSi/Si and Ni(Yb)Si/Si diodes were measured by a Keithley 2400 source meter.

RESULTS AND DISCUSSION

Influence of Yb Addition on Ni Silicidation

The sheet resistance variation with annealing temperatures is shown in Fig. 1. It can be observed that, the higher the Yb concentration, the larger the sheet resistance of the as-deposited Ni(Yb) film. Moreover, the sheet resistance of all the samples annealed between 400°C and 650°C is low. The silicide phase formed in this temperature range was identified as NiSi by XRD, as shown in Fig. 2. Thus, Fig. 1 demonstrates that there is an optimal annealing temperature window in order to obtain low-resistivity silicide even for 30% addition of Yb.

Figure 2a shows the XRD spectra of a pure Ni film on Si(001) annealed at various temperatures. Only Ni_2Si is observed from the sample annealed at 350°C, and the NiSi peak appears after annealing at 500°C or 750°C. Our observation is consistent with the reported Ni silicide phase formation.^{1,2} As

Fig. 1. Sheet resistance variation determined from silicided Ni(Yb) films on Si as a function of annealing temperatures.

Fig. 2. XRD spectra acquired from: (a) Ni(22 nm)/Si; (b) $\text{Ni}_{0.95}\text{Yb}_{0.05}$ (22 nm)/Si; (c) $\text{Ni}_{0.9}\text{Yb}_{0.1}$ (22 nm)/Si; (d) $\text{Ni}_{0.8}\text{Yb}_{0.2}$ (22 nm)/Si; and (e) $\text{Ni}_{0.7}\text{Yb}_{0.3}$ (22 nm)/Si after annealing at various temperatures in Ar for 1 min.

shown in Fig. 2b, when the Yb concentration is 5%, the intensity of the Ni_2Si peaks becomes much weaker and the full-widths at half-maximum (FWHM) of these peaks increase after 350°C annealing. Similar to the pure Ni film, only NiSi is observed from samples annealed at 500°C and 750°C. In the $\text{Ni}_{0.9}\text{Yb}_{0.1}$ film annealed at 500°C shown in Fig. 2c, in addition to the formation of NiSi, an Yb_5Si_3 peak appears from the reaction between Yb and Si but disappears after annealing at 750°C. As shown in Fig. 2d and e, similar to $\text{Ni}_{0.9}\text{Yb}_{0.1}$, the Yb_5Si_3 peak is observed after annealing at 500°C, but the Ni_2Si peaks almost disappear after annealing at 350°C. These results indicate that Yb addition may suppress Ni_2Si

Fig. 3. Micro-Raman spectra obtained from Ni(22 nm)/Si, Ni_{0.95}Yb_{0.05}(22 nm)/Si, Ni_{0.8}Yb_{0.1}(22 nm)/Si, Ni_{0.8}Yb_{0.2}(22 nm)/Si, and Ni_{0.7}Yb_{0.3}(22 nm)/Si annealed at 500°C for 1 min.

formation, although NiSi formation is still observed and low-resistance silicide films can be obtained. Therefore, comparing the XRD results in Fig. 2, Yb addition can significantly influence the formation of Ni₂Si, while that of NiSi is hardly affected. The micro-Raman spectra exhibited in Fig. 3 further confirm that a substantial amount of NiSi forms in all the samples annealed at 500°C (corresponding to the scattering peak at 212.6 cm⁻¹).

Redistribution of Yb During Silicidation

It is well known that PtSi and NiSi have the same MnP-type lattice structure and that the lattice constant of PtSi is also very close to that of NiSi.¹² Therefore, Pt is soluble in NiSi. Unlike Pt addition during Ni silicidation, the hexagonal lattice structure of YbSi₂ is quite different from the orthorhombic lattice structure of NiSi. Hence, Yb has limited solubility in NiSi and, after silicidation, Yb redistribution may occur. With regard to Yb silicidation, Si is the dominant diffusion species whereas Ni is the dominant one in Ni silicidation. During Ni(Yb) silicidation, Ni will diffuse toward the Si substrate and most of the Yb atoms will stay in their original positions. The elemental profile after annealing should show Yb accumulation in the surface layer. As shown in Fig. 4, Yb atoms are indeed observed to migrate toward the top surface of the silicide film in the Ni_{0.8}Yb_{0.2} sample after annealing at 500°C. The AES results in Fig. 5 further show that not only does NiSi form in the mid-layer but also large amounts of Yb and Si atoms are observed in the top layer. Consistent with the XRD results in Fig. 2d, it is believed that Yb₅Si₃ forms in the top layer. Both redistribution of Yb atoms in the NiSi layer and small accumulation of Yb atoms at the silicide/Si interface are observed, and may explain why there is a tail in the low-energy side of the Yb peak (labeled with a dashed circle in the inset of Fig. 4). The RBS and AES results

Fig. 4. Comparison of the RBS spectra of Ni_{0.8}Yb_{0.2}(22 nm) before and after silicidation annealing. The inset shows the magnified Yb peak in the annealed sample.

Fig. 5. AES depth profiles obtained from the Ni_{0.8}Yb_{0.2}(22 nm) sample after annealing at 500°C.

unambiguously demonstrate that, after annealing, Yb atoms in the as-deposited sample diffuse primarily to the top surface and only a small amount of Yb atoms pile up at the silicide/Si interface. However, as a rare-earth element, Yb is so active that Yb atoms aggregating in the surface layer can easily be oxidized, as shown in Fig. 5, whereas Ni is less reactive to oxygen, which has almost no influence on Ni silicidation underneath the surface layer. With the protection offered by the formed Ni silicide, Yb silicidation at the silicide/Si interface is practically not influenced by oxygen, as shown in Fig. 5.

Influence of Yb Addition on the Schottky Barrier Heights of Ni(Yb)Si/*n*-Si Diodes

Due to the small WF of Yb (~2.59 eV) and low SBH of Yb silicide (~0.27 eV), the addition of Yb to NiSi may lower the SBH on *n*-Si. The SBH of the diodes is extracted by fitting the forward *I*-*V* characteristics based on the classical thermionic emission theory¹³:

Fig. 6. Schottky barrier height cumulative probability measured from the diode samples Ni(22 nm)/n-Si, Ni_{0.95}Yb_{0.05}(22 nm)/n-Si, Ni_{0.9}Yb_{0.1}(22 nm)/n-Si, Ni_{0.8}Yb_{0.2}(22 nm)/n-Si, and Ni_{0.7}Yb_{0.3}(22 nm)/n-Si annealed at 500°C. The inset shows the average Schottky barrier height variation with different amounts of Yb.

$$I = aA^{**}T^2 \exp\left(-\frac{\phi_0}{kT}\right) \exp\left[\frac{q}{nkT}(V - IR_s)\right] \times \left\{1 - \exp\left[-\frac{q}{kT}(V - IR_s)\right]\right\}, \quad (1)$$

where a , A^{**} , ϕ_0 , k , T , n , V , and R_s are the diode area, the effective Richardson constant [112 A/cm² K² for n-Si(001)], the barrier height, the Boltzmann constant, the absolute temperature, the ideality factor, the applied voltage, and the series resistance, respectively. The I - V curves of over 20 diodes for each set of conditions were measured. According to Eq. 1, each curve is fitted to extract the barrier height ϕ_0 . Thus, for each set of conditions, there are over 20 ϕ_0 and statistical analysis is performed. Then, the accumulative probability curve for each condition is obtained as shown in Fig. 6, which indicates that the SBH of Ni(Yb)Si on n-Si (001) varies with Yb concentration.

As shown in Fig. 6, the average SBH can be effectively modulated to a value as low as 0.52 eV with the addition of 30% Yb. This is 0.12 eV lower than that measured from the pure NiSi diode sample. Even with such a low SBH, the silicide film annealed at 500°C is still within the stable silicidation temperature region, as shown in Fig. 1. In addition, the XRD results in Fig. 2e and the Raman spectra in Fig. 3 demonstrate the formation of NiSi. The SBH modulation is consistent with the fact that both the RBS results in Fig. 4 and AES results in Fig. 5 reveal accumulation of Yb atoms at the silicide/Si interface. When both NiSi and YbSi_x exist at the silicide/Si interface, the current flowing through

the contact obeys the parallel connection model. Thus, even if the SBH of NiSi/n-Si is as high as ~0.64 eV, the equivalent SBH of the whole diode will still be lower due to the lower SBH of Yb silicide (~0.27 eV).

CONCLUSION

The influence of Yb addition (up to 30%) to the Ni film on Ni silicidation has been investigated. Our results show that NiSi formation is independent of Yb addition whereas the formation of the high-resistivity Ni₂Si phase is suppressed. The optimal temperature window for the formation of stable, low-resistivity Ni(Yb)Si is between 400°C and 650°C. After annealing, most of the Yb atoms diffuse to the top layer of the film and only a small amount of Yb atoms accumulate at the silicide/Si interface, thereby resulting in the reduction of the SBH observed in the silicide/n-Si diode samples.

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