Formation of Epitaxial Nickel Monogermanide on Ge(100) by Annealing of Ni/Sn Bilayer

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Abstract

We have grown nickel monogermanide (NiGe) epitaxially on a wide range (~500 nm) of a Ge(100) surface simply by annealing a Ni/Sn bilayer. Compared with NiGe/nGe(100) diodes grown conventionally by annealing only a Ni layer, it was revealed that the reverse current in epitaxial NiGe/nGe(100) diodes was about two orders of magnitude higher, indicating that the Schottky barrier height was reduced by ~0.1 eV.

1. Introduction

To realize Ge nMOSFETs with a metal contact on the source/drain (S/D), the Fermi level pinning (FLP) of a metal in the vicinity of the charge neutrality level, close to the valence band maximum of Ge (e.g., [1, 2]), is an issue that remains to be resolved. The FLP results in a high Schottky barrier height (SBH) for metal/nGe, which causes a high contact resistance, leading to a low drive current.

One of the methods of resolving the FLP issue is to apply an epitaxially grown metal on Ge. This method enables us to decrease the interface trap density, leading to the alleviation of the FLP, i.e., the modulation of the SBH. It has been reported, for instance, that epitaxial Fe₃Si on pGe(111) can increase the SBH by ~0.18 eV [3].

Although it is desirable to form an epitaxial metal on Ge by a simple method, a special method is generally required; for instance, the above-mentioned epitaxial Fe₃Si was grown in ultra-high vacuum by molecular beam epitaxy [3].

As a simple method of growing an epitaxial metal layer, it has recently been reported that nickel monogermanide (NiGe) on Ge(100) can be grown by annealing a Ni/Zr bilayer [4]. This NiGe exhibited an approximately 50°C higher thermal stability than NiGe fabricated by annealing a Ni layer; however, the effect of epitaxially grown NiGe on the electrical characteristics has not been clarified.

In this study, we have grown NiGe epitaxially on Ge(100) simply by annealing a Ni/Sn bilayer. Attempts have recently been made to apply Sn in the form of GeSn as a semiconductor material, and the use of Sn in the S/D has the advantage of the higher electrical activation of P in has the advantage of the higher electrical activation of P in GeSn (e.g., Ge with 2.4 at.% Sn) than in Ge [5]. *J-V* measurements revealed that epitaxial NiGe/nGe enabled the reverse current to be increased by about two orders of magnitude, corresponding to an approximately 0.1 eV decrease in SBH.

2. Experiment

Ni_xGe/Ge(100) diodes were fabricated and investigated as follows. Four-inch n (p)-type Ge(100) wafers with SiO₂ isolation were used as substrates. Sn films (1-15 nm) were deposited by sputtering on the substrates, followed by Ni films (~10 nm). Then, rapid thermal annealing was per-formed at 350°C in N₂ for 1 min. The annealed substrates were treated with HCl to remove unreacted Ni. For comparison, NiGe grown conventionally by annealing a single Ni layer on Ge(100) [NiGe(ref.)] was also prepared for reference. The compositions were analyzed by transmission electron microscopy (TEM) and energy-dispersive x-ray spectroscopy (EDX), and the structures were determined from TEM images and by fast Fourier transform (FFT) of the TEM images. The J-V characteristics were measured to evaluate the SBH φ , which was estimated by theoretical fitting to the equation for the Schottky current [6] at 300 K, $J=A^*T^2 \exp(-q\varphi/k_BT)[\exp(qV/k_BT)-1]$ (1).

3. Results and Discussion

By annealing Ni/Sn bilayers with various Sn thicknesses, we found that for an appropriate Sn thickness (1-5 nm),

 Ni_x Ge layers were grown epitaxially on Ge(100), according to the results of TEM observation [Fig. 1(b)]. The Ni_xGe/Ge structure had a smoother interface and larger grains (~500 nm in the range of TEM observation) than NiGe(ref.) [Fig. 1(a)]. In the case of a thicker Sn layer, Ni_xGe had a rougher interface and was formed discontinuously [Fig. 1(c)].

The composition of Ni_xGe was mainly x = 1, whereas some Ni_xGe with x = 2 was formed near the surface, and Sn mostly existed around the Ni_xGe surface and $Ni_xGe/Ge(100)$ interface. The composition of the Ni_xGe at the four points in Fig. 2 was determined by EDX analysis (Fig. 3) and is shown in Fig. 4. The composition in the middle part (point 3 in Fig. 2) of Ni_xGe was \sim 54 at.% Ni and \sim 46 at.% Ge, i.e., the Ni/Ge ratio was almost unity. Hardly any Sn was detected in the same middle part, e.g., 0.38 at.% at point 3. On the other hand, the composition of some of the Ni_xGe existing near the surface with the darker contrast in the TEM images (points 1 and 2) had a Ni/Ge ratio of \sim 2. Sn was mostly detected near the surface, e.g., 1.44 (0.61) at.% at point 1 (point 2). The profiles of a line scan obtained by EDX analysis revealed the existence of Sn around the Ni_xGe/Ge(100) interface as well as near the Ni_xGe surface (Fig. 5), and that Sn existed near the surface irrespective of the composition of Ni_xGe.

We confirmed that the main structure of Ni_xGe was the same as that of the NiGe. The FFT of the TEM image (Fig. 2) produced the spot patterns shown in Fig. 6, the results of which are shown in Table 1. Spot 1 (spot 2) in Fig. 6(c) has a lattice plane spacing of d = 0.296 nm (0.196 nm), and the angle θ between the two planes is 29.0°. From the data on the structure and composition (Ni/Ge ratio = ~1), it was clarified that the grown film was orthorhombic nickel monogermanide (NiGe) with $d_{\text{NiGe}}(011) = 0.289$ nm, $d_{\text{NiGe}}(121) = 0.199$ nm, and the angle between the two planes of $\theta = 27.6^{\circ}$. Similarly, we confirmed that the Ni_xGe existing near the surface (points 1 and 2) was dinickel ger-manide (Ni_2Ge). Because NiGe rather than Ni_2Ge was the main structure, the epitaxially grown Ni_xGe is suitable for use as a contact metal since the resistivity of Ni_xGe increases with Ni composition [7].

Our NiGe layers were grown on Ge(100) with matching lattice spacing at the NiGe/Ge(100) interface (Fig. 7). Although $d_{\text{NiGe}}(121)$ was 0.199 nm as described above, $d_{\text{Ge}}(011)$ was 0.402 nm. The angle θ formed by $d_{\text{Ge}}(011)$ and $d_{\text{NiGe}}(121)$ in the TEM image was estimated to be ~9°.

These values satisfy the relation $d_{\text{Ge}}(011) \cos \theta = 2 d_{\text{NiGe}}(121)$ (2). Thus, the NiGe layers were grown epitaxially on Ge(100). A possible model for the formation of epitaxial Ni-Ge/Ge(100) using a Ni/Sn bilayer is that the Sn layer acts as a diffusion-controlling layer [8] in the reaction between Ni and Ge(100). Ni passes through the Sn layer by diffu-sion, reaches Ge(100), and forms NiGe. This process would result in a slow reaction between Ni and Ge(100), leading to the epitaxial growth of NiGe on Ge(100). The reason why Sn was mainly detected near the NiGe surface is that the layers of Sn and Ni are exchanged according to the model. The existence of Ni_2Ge near the surface is probably related to the fact that Ni_2Ge nucleates first in the Ni-Ge

system [9]. The J-V characteristics of epitaxial NiGe/pGe(100) exhibited ohmic behavior, indicating that not the Schottky but substrate-limited current was dominant current [Fig. 8(b)]

On the other hand, the J-V characteristics of epitaxial NiGe/nGe(100) exhibited a higher reverse current than those of NiGe(ref.)/nGe(100), indicating a decrease in SBH [Fig. 8(a)]. The SBH estimated using Eq. (1) was 0.50-0.55 eV, ~0.1 eV less than that of NiGe(ref.)/*n*Ge(100), assuming that the increase in current was only due to the modulation of the SBH. Thus, epitaxially grown NiGe on nGe(100) decreased the SBH.

It is expected that by optimizing the epitaxial Ni-Ge/nGe(100), the SBH can be further reduced.

4. Summary

We grew epitaxial NiGe layers on a wide range (\sim 500 nm) of a Ge(100) surface by annealing a Ni/Sn bilayer. Compared with NiGe/nGe(100) diodes formed conventionally by annealing only a Ni layer, it was revealed that the reverse current in epitaxial NiGe/nGe(100) diodes was about two orders of magnitude higher, indicating that the SBH could be reduced by ~0.1 eV.



FIG. 1: TEM images of Ni_xGe/Ge(100) fabricated by annealing Ni(10 nm)/Sn bilayer on Ge(100) at 350°C in N₂ for 1 min. The thicknesses of the Sn layers were (a) 0 nm, (b) 1-5 nm, and (c) 12-15 nm.

0.61

36.39

63.01

2 Point

FIG. 4: Compositions at four

.44

35.54

63.02

1

10²

10¹

 10°

10¹ (A/cm²) 10¹ (A/cm²)

10

10

10

0.38

45.7

53.92

0.4 Sn

Ge

46.3

53.3 Ni

4



FIG. 3: TEM-EDX spectra at points 1-4 in Ni_xGe layer (Fig. 2).



FIG. 6: Spot patterns obtained from FFT of TEM image (Fig. 2), where (a)-(d) indicate spot patterns of Ni_xGe at points 1-4, respectively. (a) 10³



FIG. 7: TEM image of NiGe fabricated with Ni/Sn bilayer. The enlarged view of Fig. 1(b).

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FIG. 2: Positions of TEM-EDX analysis of Ni_xGe layer [Fig. 1(b)].



analysis of NixGe (Fig. 2).

Table. 1: Lattice plane spacing and angle between two planes of Ni_xGe at points 1-4 (Fig. 2) determined from FFT (Fig. 5). The values for NiGe and Ni2Ge are from the JCPDS database.



by annealing Ni/Sn bilayers.