MORPHOLOGY OF NISI FILM ON SI(100): ROLE OF THE INTERFACE STRAIN.

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ABSTRACT

The role of strain on the thermal stability of NiSi has been studied by deposition and annealing of Ni on strained and relaxed Si(100) n-type substrates. Strained Si substrates have been produced by depositing a pseudomorphic silicon film on top of a 3000 Å thick relaxed $Si_{0.8}Ge_{0.2}$ film. Raman spectroscopy has proved the top silicon film to be strained. The presence of the characteristic hatch-cross pattern has been confirmed by Atomic Force Microscopy (AFM). Scanning electron microscopy (SEM) and Photoelectron emission microscopy (PEEM) show that the islanding of the NiSi film appears at lower temperature on the bulk silicon substrate (600°C) than on the strained silicon substrate (700°C). The improved thermal stability of NiSi on strained Si can be explained by the difference in relative interface energy of NiSi on strained and relaxed silicon. The thermal expansion coefficient of Ni being 3 times larger than that of Si, NiSi is in compression on Si at 500°C already. The correlation of this compression state with the lattice parameters of bulk and strained Si (100) produces an increased NiSi islanding probability on bulk Si (100) with respect to strained Si.

INTRODUCTION

Silicides used in VLSI circuits as contact materials to the source and drain areas must show a metal-like conductivity while sustaining the high temperature thermal treatment used in manufacturing. Nickel monosilicide (NiSi) is one of the most promising candidate for the next generation of deep sub-micron integrated circuits. The formation of Ni silicides on Si has been shown to start with Ni_2Si formation around 200°C followed by NiSi formation around 500°C and finally by $NiSi_2$ formation, which is the final phase, growing epitaxially on Si (100), (110) and (111) around 800°C [1]. As the sheet resistivity of the silicide is increasing from 20 $\mu\Omega$cm to 50 $\mu\Omega$cm with the transition from NiSi to $NiSi_2$, the thermal stability of the NiSi is of primary importance for technical applications.

The sheet resistance of Ni silicides depends on the phase transition from NiSi to $NiSi_2$ and on the morphology of the NiSi film. The morphology of the NiSi influence its resistivity as the resistivity of a defective silicide film or a system of islands is higher than that of a perfect silicide film [2]. The morphology is usually characterized by SEM [3], AFM [4] and TEM [5].

In this paper, the influence of the Si substrate strain on the thermal stability of the NiSi will be presented. Variations of morphology measured by SEM and PEEM will be explained in term of interface strain.

EXPERIMENT

Thin films of Ni (100 Å thick) have been deposited on n-type Si (100) and strained silicon substrates by electron beam evaporation. The strained silicon substrates have been produced by deposition of a pseudomorphic silicon film on top of a 3000 Å thick relaxed $Si_{0.8}Ge_{0.2}$ film grown by Molecular Beam Epitaxy (MBE) at 550°C in an Simba 2 system with a base pressure of $5x10^{-10}$ Torr. Subsequently to Ni deposition, the samples were annealed in situ for 20 min at temperatures ranging from 300°C to 1000°C (controlled by thermocouple). XPS measurements have been performed in situ in a VG Clam II spectrometer.
AFM measurements in air have been performed with a M5 Park Scientific STM/AFM and Raman spectroscopy has been performed with an ISA Jobin Yvon U1000. SEM images of the NiSi films have been taken in a JEOL JSM-6400F.
Photoelectron Emission Microscopy (PEEM) has been performed in a PEEM III from Elmitech. The sample is illuminated by a Hg lamp with an energy cutoff at 5.1 eV and placed at a negative DC potential of 20 kV. An image is formed by emission of photoelectrons, depending on the photo-threshold of the sample surface material.

RESULTS

Strained Si substrates have been produced by deposition of Si on top of a 3000 Å thick relaxed $Si_{0.8}Ge_{0.2}$ film. Relaxed Si_xGe_{1-x} alloys grown on Si(100) show a <110> hatch-crossed pattern of dislocation lines [6]. Figure 1 shows the substrate surface after the Si deposition. The Si film presents the same morphology as the $Si_{0.8}Ge_{0.2}$ substrate proving that the relaxation of the lattice is maintained. As the lattice parameter of $Si_{0.8}Ge_{0.2}$ (5.47 Å) is 1% bigger than the lattice parameter of Si (5.43 Å), the Si layer is under tensile stress.

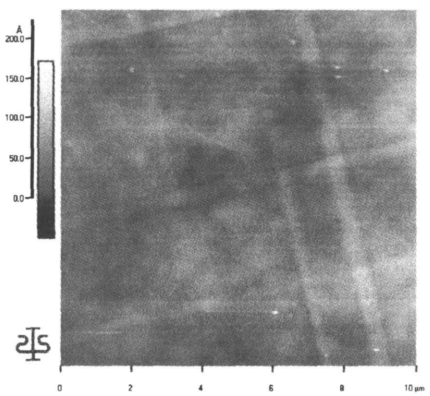

Figure 1: AFM image of the strained silicon surface showing the characteristic <110> hatch-crossed pattern. The dislocation lines are ca. 25 nm wide and distant of 1 to 4 μm.

Raman spectroscopy has been performed on the Si layer in order to prove the tensile strain of the Si. Fits of the Raman peak show the main Si-Si component at 520 cm^{-1} due to the bulk Si substrate, one component at 513 cm^{-1} due to the Si-Si bond in the tensile-strained Si layer and a

multiple component around 506 cm^{-1} from the Si-Si bond in the $Si_{0.8}Ge_{0.2}$ pseudo-substrate as predicted by Weber et al. in [7].
A 100 Å thick Ni film has been deposited on 400 Å thick strained Si layers. After in situ annealing at temperatures ranging from RT to 1000°C, XPS has shown a stable NiSi phase up to an annealing temperature of 900°C.
SEM however shows morphology instabilities (Fig. 2 (a) to (d)) before the phase transition. After an annealing at 700°C, the NiSi grown on strained Si forms a perfect film with no islanding (Fig 2 (a)) when the NiSi grown on bulk Si(100) shows voids at 600°C already (Fig. 2 (b)). After annealing at 850°C, both NiSi films show a voids density which is however larger in the case of NiSi on strained Si (Fig. 2 (c) and (d)).

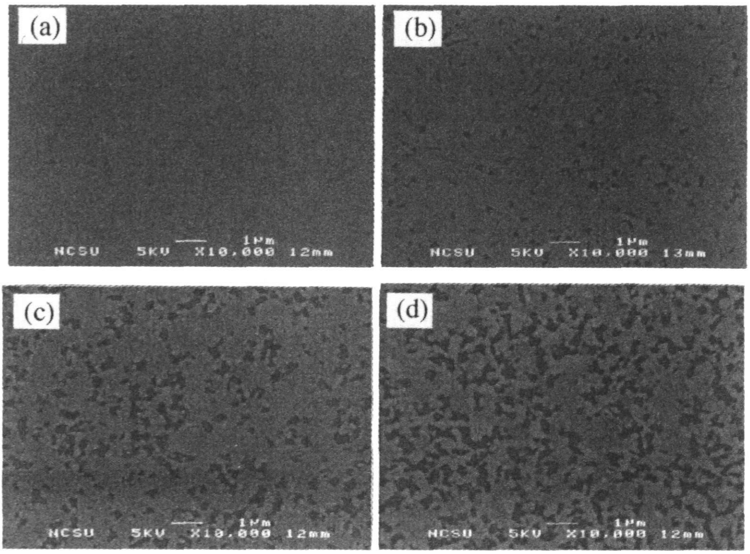

Figure 2: SEM images of (a) Ni on strained Si after annealing at 700°C (b) Ni on bulk Si (100) after annealing at 600°C (c) Ni on strained Si after annealing at 850°C (d) Ni on bulk Si (100) after annealing at 850°C. NiSi is in gray and Si in black.

The delayed morphology changes are confirmed by PEEM measurements which allow a continuous observation of the modifications with the increasing temperature. Fig. 3 shows 50 μm diameter fields of view of NiSi on bulk Si (100) and strained Si. In our case, the contrast is rather produced by topography variations than by variations of the chemical composition of the investigated sample. This has been confirmed by XPS measurements. The islanding of NiSi starts at 625°C on bulk Si (100) (Fig. 3 (b)) and at 730°C (Fig. 3 (a)) on strained Si. We notice bigger islands on strained Si. Then the density of islands is quickly increasing on bulk Si (100), with a decrease in the islands size (Fig. 3 (d)). However, the NiSi islands density is increasing only at 850°C on strained Si (Fig. 3 (c)).

Islanding depends on the surface energies of the substrate and the overlayer. If the surface free energy of the overlayer is bigger than the surface free energy of the substrate, the overlayer forms 3-dimensional clusters (Volmer-Weber growth) [8]. If the surface energy of the overlayer is smaller than the surface energy of the substrate, a film is growing (layer-by-layer growth) [9]. With a value for the surface free energy of NiSi between 2450 mJm^{-2} (Ni) and 1250 mJm^{-2} (Si (100)), NiSi will form islands on Si.

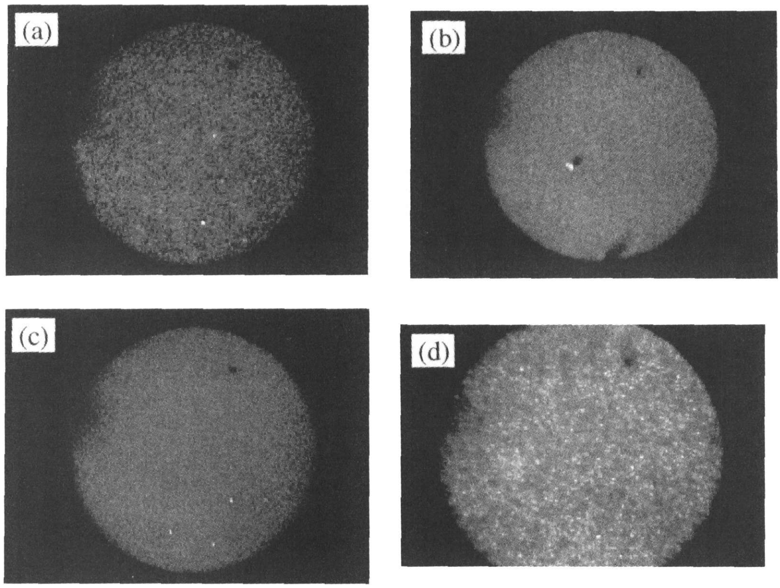

Figure 3: 50 μm in diameter PEEM fields of view of (a) Ni on strained Si after annealing at 730°C (b) Ni on bulk Si (100) after annealing at 625°C (c) Ni on strained Si after annealing at 850°C (d) Ni on bulk Si (100) after annealing at 850°C.

Surface stress is the sum of the surface free energy and an elastic strain term [10]. As the strain energy is part of the surface energy [11], the role of the interface stress in the islanding is not negligible either. Stress is mainly due to lattice mismatch which already exist at room temperature (NiSi: orthorhombic P structure, a= 5.23 Å, Si: diamond structure, a=5.43 Å, strained Si: a= 5.47 Å) and varies with temperature due to different thermal expansion coefficients.
In our case, morphology changes appear after annealing of the sample at 600°C i.e. after the formation of NiSi. At such temperature, NiSi is in compression because its expansion coefficient (Ni: 15×10^{-6} K^{-1}) is higher than that of the Si (3×10^{-6} K^{-1})[12]. As the lattice parameter of strained Si on $Si_{0.8}Ge_{0.2}$ is 1% larger than that of bulk Si (100), the interface stress between the NiSi film and the substrate is lower in the case of a strained Si substrate. Islanding of the overlayer requires therefore a higher annealing temperature on strained Si inducing a improved thermal stability of the NiSi film.

CONCLUSIONS

By depositing Si on top of a relaxed $Si_{0.8}Ge_{0.2}$ pseudo-substrate, we produced a strained Si (100) substrate. NiSi grown on such a substrate has proved to be thermally more stable than NiSi grown on bulk Si (100). Influence of this stability on sheet resistance variation are discussed in [13]. SEM and PEEM investigations have proved the NiSi islanding to be delayed by 100°C on strained Si. The stress at the interface produced by thermal expansion of the NiSi during the annealing process is lower in the case of the strained Si substrate because of the substrate larger lattice parameter. Islanding of NiSi on strained Si requires therefore a higher annealing temperature explaining the improved NiSi thermal stability.

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References

[1] F.M. d'Heurle, C.S. Petersson, J.E.E. Baglin, S.J. LaPlaca and C.Y. Wong, J. Appl. Phys., **55** (12), 4208 (1984).
[2] N. Artunc, Z.Z. Ozturk, J. Physics Cond. Mat., **5**, 559 (1993).
[3] S. Ino, T. Yamanaka, S. Ito, Surface Science, **283**, 319 (1993).
[4] J.T. Mayer and E. Garfunkel, Nanostructured Materials, Vol. 4, No 3, 275 (1994), ed. Elsevier Science Ltd.
[5] Y.Z. Feng, Z.Q. Wu, J. Mater. Sci. Lett., **15**, 2000 (1996).
[6] J. Welser, J.L. Hoyt and J.F. Gibbons, Jpn. J. Appl. Phys., **33**, 2419 (1994).
[7] J. Welser, J.L. Hoyt, S. Takagi and J.F. Gibbons, IEEE, IEDM-94, 373 (1994).
[8] M. Volmer and A. Weber, Z. Phys. Chem, **119**, 277 (1926).
[9] F.C. Frank and J.H. van der Merwe, Proc.R.Soc. London Ser. A, **198**, 205 (1949).
[10] W.N. Unertl, Handbook of Surface Science, Physical structure, Vol.1, ed. Elsevier (1996).
[11] J.A. Floro, C.V. Thompson, R. Carel and P. Bristowe, J. Mater. Res. **9** (9), 2411 (1994).
[12] S. Nygren, D. Caffin, M. Oestling and F.M. d'Heurle, Appl. Surf. Science, **53**, 87 (1991).
[13] E. Maillard-Schaller, B.I. Boyanov, S. English and R.J. Nemanich, submitted to J. Appl. Phys. (April 1998).