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On epitaxy of ultrathin $\text{Ni}_{1-x}\text{Pt}_x$ silicide films on Si(001)

Jun Lu,^{1*} Jun Luo,^{2,3} Shi-Li Zhang^{2,3,4*}, Mikael Östling,³ and Lars Hultman¹

¹Department of Physics, Chemistry and Biology, Linköping University, 58183 Linköping, Sweden

²State Key Lab of ASIC & Systems, Fudan University, Shanghai 200433, China

³School of Information and Communication Technology, Royal Institute of Technology, 16440 Kista Sweden

⁴Solid-State Electronics, The Ångström Laboratory, Uppsala University, Box 534, 75121 Uppsala Sweden

Abstract

Epitaxial Ni(Pt)Si_{2-y} ($y < 1$) films readily grow upon thermal treatment of 2-nm thick Ni and $\text{Ni}_{0.96}\text{Pt}_{0.04}$ films deposited on Si(001). For annealing at 500 °C, the films are 5.4-5.6 nm thick with 61-70 $\mu\Omega\text{cm}$ in resistivity. At 750 °C, the epitaxial Ni(Pt)Si_{2-y} films become 6.1-6.2 nm thick with a resistivity of 42-44 $\mu\Omega\text{cm}$. Structural analysis reveals twins, facet wedges, and thickness inhomogeneities in the films grown at 500 °C. For the higher temperature, an almost defect-free NiSi_{2-y} film with flat and sharp interface is formed. The presence of Pt makes the aforementioned imperfections more persistent.

E-mail addresses: junlu@ifm.liu.se; shili.zhang@angstrom.uu.se

Introduction

Metal silicides constitute an important class of electronic materials for electrical contact and local interconnect in advanced complementary metal-oxide-semiconductor (CMOS).^{1,2} In the state-of-the-art CMOS technology, NiSi is the most widely used silicide primarily due to its low specific resistivity. During device fabrication, the NiSi film formation usually proceeds by annealing a pre-deposited Ni film on a patterned Si substrate. Since NiSi has a low melting point at 990 °C, the morphological stability of NiSi thin films has been a main concern for device performance and reliability. In the Ni-Si binary system, several phases exist at room temperature. The phase formation sequence in Ni/Si diffusion couples has recently been found to alter when pre-deposited Ni films on Si substrate are below 4 nm in thickness,^{3,4} and similar observations were in fact made in early 1980's.⁵⁻⁷ For Ni films thicker than 4 nm, the phase formation follows the usual route and polycrystalline NiSi films form between 400 and 750 °C. For Ni films with 4 nm thickness or thinner, epitaxial NiSi₂ films readily grow and exhibit extraordinary morphological stability up to 800 °C. Surface energy was discussed as the cause responsible for the distinct behavior in phase formation and morphological stability.³

Addition of Pt to NiSi has been shown to improve the morphological stability of the silicide contact,⁸ making this process a standard practice today. The physics behind this phenomenon is a higher melting point of the ternary alloy (Ni,Pt)Si than that of NiSi, thereby decreasing the atomic diffusivity in the silicide film and delaying the film agglomeration to higher temperatures. The energy gain due to entropy of mixing in the formation of (Ni,Pt)Si has an added advantage by significantly delaying the formation of NiSi₂ that has a resistivity about 2-3 times that for NiSi.⁹ However, the phase formation in the presence of Pt has again been found to be thickness dependent^{3,4} and epitaxial Ni(Pt)Si_{2-y} does form when the initial Ni(Pt) thickness is 2 nm or below. In order to shed more light on the kinetics and morphology

of the epitaxial silicide films, we have prepared Ni and Ni_{0.96}Pt_{0.04} films using magnetron sputtering and studied the reactions by means of electron microscopy. Extensive HRTEM studies are correlated to resistance measurement data of NiSi_{2-y} and Ni(Pt)Si_{2-y} films in the present work.

Experimental

Silicon (001) wafers, 100 mm in diameter and *p*-type with a resistivity of 20-40 Ω-cm, were used as substrate. After standard wafer cleaning and removal of native oxide in dilute HF solution (5% in H₂O solution) for 30 s, the wafers were immediately loaded into a dual-magnetron sputtering deposition chamber with a base pressure of 6×10⁻⁸ Pa to deposit 2-nm thick Ni or Ni_{0.96}Pt_{0.04} films at room temperature using elemental targets of Ni and Pt. The composition and thickness of the metal films were determined by means of Rutherford Backscattering Spectrometry. The thickness was also monitored using a crystal oscillator during the deposition. In order to double-check the thickness, small angle X-ray reflectivity method was performed. The results of these two measurement methods were consistent. The spread of sheet resistance of silicide films over a whole wafer is small indicating a quite uniform Ni coverage. No *in-situ* clean was used prior to metal deposition. The pressure, power, and substrate temperature for Ni sputtering were 0.6 Pa, 37 W, and 20 °C, respectively. For Pt deposition, these parameters were 0.6 Pa, 18 W, and 20 °C. After metal deposition, the wafers were sliced to 2 cm × 2 cm pieces. The samples were then annealed in N₂ at 450 to 850 °C each for 30 s, in a rapid thermal processing (RTP) chamber. Sheet resistance was measured using a four-point probe. Cross-sectional high resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), and energy dispersive spectroscopy (EDS) were carried out on a Tecnai G2 UT instrument operated at 200 kV with a 0.19 nm point resolution on selected samples, prepared by the conventional ion beam milling method.

Results and discussion

The sheet resistance measurement results are shown in Fig. 1. Both samples show a similar trend with a sharp decrease in resistance between 450 and 500 °C. Thereafter, a steady

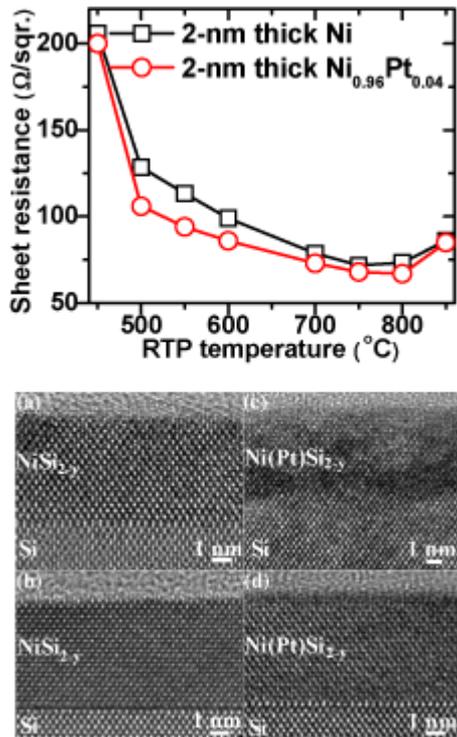


Fig. 1 – Top: Sheet resistance versus RTP temperature for the silicide formation starting from 2-nm thick Ni and Ni_{0.96}Pt_{0.04} films. Bottom: HRTEM images in the insets: (a) – NiSi_{2-y} formation at 500 °C, (b) – NiSi_{2-y} formation at 750 °C, (c) – Ni(Pt)Si_{2-y} formation at 500 °C, and (d) – Ni(Pt)Si_{2-y} formation at 750 °C.

decrease, almost linearly, with annealing temperature from 500 to 750 °C is found. The HRTEM images and the corresponding electron diffraction patterns (not shown) can be indexed by the NiSi₂ phase with the CaF₂ structure. According to the HRTEM data (insets in Fig. 1), the thickness of the silicide films (5.4-6.2 nm) is about 15-25% thinner than the expected thickness (7.2 nm) of a stoichiometric NiSi₂ according to the initial Ni and Ni_{0.96}Pt_{0.04} film thickness (2 nm). The thickness deviation could be due to non-stoichiometry of the films and consequently the epitaxial silicide film should be expressed as Ni(Pt)Si_{2-y} with y=0.3-0.5. The average thicknesses of the films measured from the HRTEM images are listed in Table I. Apparently, silicidation at the higher (RTP) temperature has led to a 10-15% increase in film thickness. The higher RTP temperature also yields a 30-35% decrease in resistivity. Surface scattering in this range of film thickness could be a contributor to the

resistivity decrease. The HRTEM analysis below shows that the quality of epitaxy is substantially improved by raising the RTP temperature.

The dependence of epitaxy quality on temperature is anticipated, and several interesting details are discussed as follows. As shown in inset (a) of Fig. 1, the epitaxial relationship between the film grown at 500 °C and the Si(001) substrate is $\text{NiSi}_{2-y}(001)[1-10]//\text{Si}(001)[1-10]$. The NiSi_{2-y} film has thus the so-called “Type A” structure,^{5,6} as it has the same crystallographic orientation as the Si substrate. The $\text{NiSi}_{2-y}/\text{Si}$ interface formed at 500 °C can be as sharp and flat as seen in inset (a) of Fig. 1 at some regions, but the NiSi_{2-y} film is far from uniform. A twin structure with a large number of defects is found in Fig. 2(a) for the NiSi_{2-y} film grown at 500 °C. The size of the twin is as large as a few nanometers. The twin structure is verified by the corresponding fast Fourier transform (FFT) pattern with the relationship $(111)[-110]_{\text{twin}}// (111)[1-10]_{\text{Si}(001)}$. Such twins have been reported to easily grow on Si(111) surface, and are often denoted as “Type B” structure^{5,6} since it shares the Si surface normal axis, but rotates 180° around the axis. While the Si(001) surface is favorable for growth of the Type A structure, a non-flat Ni/Si(001) or $\text{NiSi}_{2-y}/\text{Si}(001)$ interface could yield facets with (111) planes and thus provide a nucleation site for the twin growth. A further example of the twin structure as well as non-uniformity with the NiSi_{2-y} film grown at 500 °C is shown in Fig. 2(b).

For the NiSi_{2-y} film grown at 750 °C, an atomically flat interface to the Si(001) substrate is observed in inset (b) of Fig. 1. Although traces of twins were present in the film, no facet wedge structure growing into the substrate was found. The flat $\text{NiSi}_{2-y}/\text{Si}$ interface indicates the growth of a dislocation-free film, which was confirmed by both top-view bright field and dark-field TEM imaging obtained from the $(200)_{\text{NiSi}_{2-y}}$ reflection (results not shown). The NiSi_{2-y} film grown at 750 °C is imperfect and an interface step as marked in Fig. 2(c). The step marked by a black arrow at the film surface is an extension of the interface step since

they share the same (111) plane. Thus, the defect initiated at the $\text{NiSi}_{2-y}/\text{Si}$ interface propagates through the film without causing lattice defects inside the film.

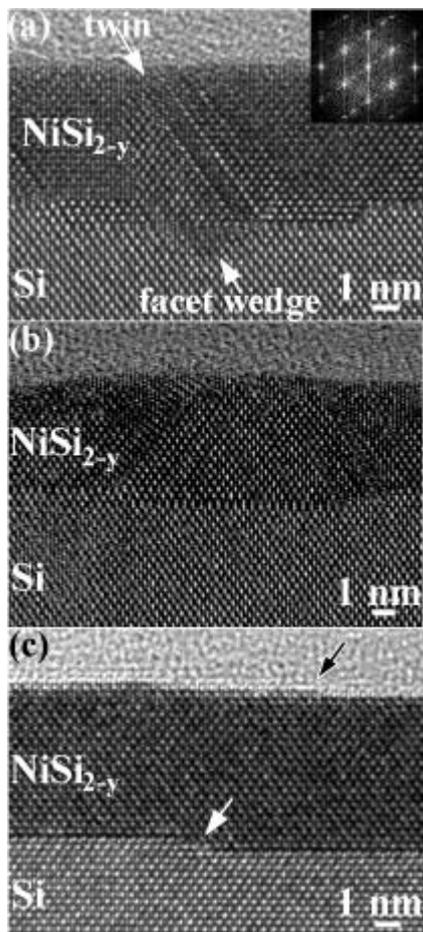


Fig. 2 – HRTEM images for NiSi_{2-y} films formed at (a) and (b) 500 °C, and (c) 750 °C.

The formation of epitaxial Ni(Pt)Si_{2-y} films was observed by HRTEM as shown as inserts (c) and (d) of Fig. 1. A higher density of defects in the ternary silicide film as shown in Fig. 3, compared to that in the NiSi_{2-y} film, is evident, likely due to a reduced atomic diffusion in the Ni(Pt)Si_{2-y} . Platinum tends to segregate at the two surfaces of growing Ni-silicide films,^{10,11} and a recent *in situ* Rutherford backscattering spectroscopy analysis reveals how the surface/interface segregation of Pt evolves during the Ni-silicidation.¹² In the present work, STEM-EDS line scan across the silicide layer was performed. The STEM images and the corresponding EDS composition profiles in Fig. 4 not only confirm the Pt segregation at the

two surfaces of the grown Ni(Pt)Si_{2-y} film, but more importantly provide an excellent correlation between a defective film and the interfacial Pt segregation at microscopic scale. When Pt is only found at the top surface, cf. Figs. 4(a) and (b), the Ni(Pt)Si_{2-y} film is found uniform in thickness. When Pt is also present at the interface, cf. Figs. 4(c) and (d), non-uniform distribution of Pt yields a thickness-inhomogeneous Ni(Pt)Si_{2-y} film and local thinning is evident.

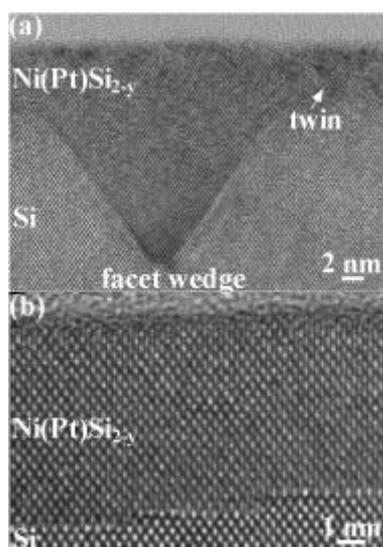


Fig. 3 – HRTEM images for Ni(Pt)Si_{2-y} films formed at (a) 500 °C and (b) 750 °C.

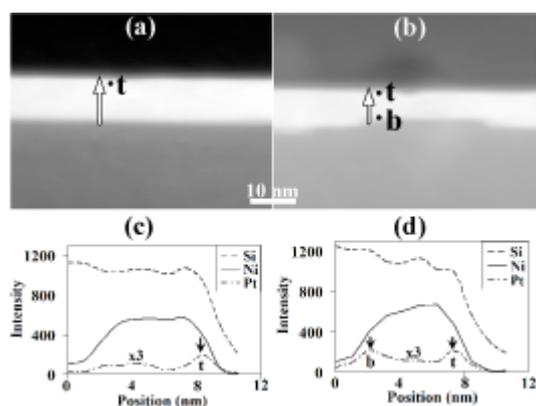


Fig. 4 – STEM-EDS line scans for the Ni(Pt)Si_{2-y} film formed at 750 °C. For a thickness-uniform region, (a) STEM image and (b) the corresponding EDS composition profile scanned from the bottom with the surface Pt marked with “t”. For a thickness-inhomogeneous region, (c) STEM image and (d) the corresponding EDS composition profile scanned from the bottom with the surface and interface Pt marked with “t” and “b,” respectively. To compare with the Si and Ni signals, the intensity of Pt signal is multiplied by 3.

Conclusions

In summary, epitaxially aligned Ni(Pt)Si_{2-y} films in the thickness range of 5.4-6.2 nm and with a low resistivity of 42-44 μΩcm have been shown to readily form on Si(001) substrates. Such films are morphologically stable up to 800 °C. While the density of defects such as twins and facet wedges in the films can be minimized by increasing the formation temperature, they are much more persistent in Ni(Pt)Si_{2-y}.

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Table I – RTP temperature (30 s for all) and properties of resultant epitaxial silicide films (average data, see text), starting from 2 nm thick Ni or Ni_{0.96}Pt_{0.04}.

Metals	Ni		Ni _{0.96} Pt _{0.04}	
RTP temperature (°C)	500	750	500	750
NiSi _{2-y} /Ni(Pt)Si _{2-y} (nm)	5.4	6.1	5.6	6.2
Specific resistivity (μΩ-cm)	69.4	43.8	61.4	42.2

