Chapter 5 Metal-Semiconductor Compound Contacts to Nanowire Transistors



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5.1 Introduction

Semiconductor nanowires [1–4] are promising building blocks for next-generation ultrascaled devices for electronic [5–7] and optoelectronic [8–10] applications. An important aspect for the development, maturity, and efficiency of these ultrascaled devices is the detailed understanding of and control over the phase transformation that accompanies the formation of their compound contacts for lithography-free self-aligned gate design [11, 12]. The term "compound" here refers to the formed phases that have fixed stoichiometry between metal and semiconductor elements, to be distinguished from the broader "alloy" term for phases that may include nonstoichiometric or amorphous structure. This distinction is important because the formation of a low resistance, crystalline, and thermally stable compound contact is most preferred for realizing reliable functionality in ultrascaled semiconductor transistors. Usually, the phase of compound contact and its interfacial property with semiconductor nanowire (NW) can largely affect the band alignment and charge injection in NW channels. This demands the detailed studies of the metal-semiconductor solid-state reactions, including the formed compound phases,

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reaction kinetics, and their correlation to the device performances. In this book chapter, we provide a thorough discussion of these three topics.

5.2 Phases of Metal-Semiconductor Compound Contacts

Deep knowledge on the material sciences of metal-semiconductor compound contacts is critical for achieving desired device performance for NW transistors. The development of these high-fidelity contacts should start with an understanding of the phases of the naturally or thermally formed metallic compound contacts at the metalsemiconductor junction. Ideally, a crystalline compound with low-resistivity phase is preferred as contact to a NW transistor. It has also been noticed that atomically abrupt interfaces between metallic contacts and semiconductor can help reduce the surface Fermi-level pinning and control the Schottky barrier height (SBH) [13], which is especially critical for small bandgap semiconductors (e.g., Ge, III–V, etc.) that have small electronegativity difference and a generally low index of interface behavior [14] with high density of surface and metal-induced gap states. Moreover, interfacial correlations between compound contact and semiconductor nanowire channel can further alter the electrical performances by exerted strains. Therefore, a thorough understanding of the phases and interfacial relationships for those compound contacts is needed.

Several precedent reviews [15–19] have extensively discussed the solid-state reactions between various metals and semiconductor NWs. In this chapter, we will not cover all the compound contacts to NWs with different metal-semiconductor combinations, but rather focus on several critical ones of practical importance for devices and provide in-depth discussions on the phase selection rules in low-dimensional NW semiconductor channels. A table (Table 5.3) can be found at end of this section, which summarizes the compound contacts surveyed in this chapter.

5.2.1 Metal Silicide in Si NWs

Metal silicides have long been used as the standard contacts to conventional Si CMOS devices, and the semiconductor manufacturing lines witnessed the transition from TiSi₂ to CoSi₂ and to NiSi technology due to the considerations of contact resistance and dimensional scaling [20, 21]. NiSi has demonstrated its superior properties to other candidates, such as reduced thermal budget, low resistivity, less Si consumption for ultrathin device layer, and controlled silicide formation by Ni diffusion [22–24]. Therefore, nickelide silicide shows great promise to serve as a standard contact to Si NW transistors and has been most widely studied.

In the nickel silicide reaction on thin film or bulk Si structures, δ -Ni₂Si is the single phase formed at low temperature around 200 °C, transformed to NiSi phase at



Fig. 5.1 TEM images of nickel silicide formation in a Si NW. (a) TEM image showing the phases that coexist during solid-state reaction between Ni pad and Si NW at 425 °C. The inserted diffraction patterns (from left to right) represent Ni₃₁Si₁₂, δ -Ni₂Si, and θ -Ni₂Si phases with their zone axes of [010, 120, 212], respectively. Scale bar is 400 nm. (b) and (c) TEM images with higher magnification at NiSi₂ and Si interfaces. Despite the Si NW growth orientations of [112] or [111], the reaction front is on a Si (111) plane. Scale bars are 20 nm and 50 nm, respectively. (Reproduced with permission from Ref. [26]. Copyright 2012 American Chemical Society)

temperatures above 350 °C, and finally converted into NiSi₂ phase at above 750 °C [25]. However, in Si NW channels, the phase sequences are dramatically different. As shown in Fig. 5.1a, several phases exist simultaneously upon thermal annealing of Ni pad on top of a Si NW, including NiSi₂ as the leading and interfacial phase in direct contact with the pristine Si NW, followed by θ -Ni₂Si, δ -Ni₂Si, and Ni₃₁Si₁₂ [26]. This phase sequence is generally observed under a broad range of reaction temperatures, 300~650 °C, with some minor differences (presence or absence) in some of the Ni-rich intermediate phases [27–29]. The leading phase, NiSi₂, has the same crystal family as pristine Si with very similar lattice constant, leading to nearly zero volume changes after NiSi₂ phase formation. This NiSi₂ phase grows on the low-energy Si (111) facets independent of the growth orientation of Si NW

(as shown in Fig. 5.1b, c), and the interfacial correlation is NiSi₂(111)llSi(111) and NiSi₂[-110]llSi[-110] is applicable to the various studied orientations. Near the Ni contact pad, more Ni-rich silicide phases appear, and their crystal structures, lattice constants, and volume expansions are all summarized in Table 5.3. It is worth noting that NiSi₂ is the phase that is thermodynamically favored to form at high temperature when Ni reacts with planar thin film or bulk Si and that θ -Ni₂Si is stable above 825 °C according to the Ni/Si phase diagram. In the following part of this section, two questions will be addressed: (1) why are the phase sequences formed in Si NW be manipulated?

To address these questions and to understand the coexistence of multiple phases (including high-temperature phases, NiSi₂ and θ -Ni₂Si) instead of expected NiSi phase at reaction temperatures of 300~650 °C, one need to consider the different thermodynamic treatments in two extremes of relative material abundance of the binary solid-state reactants. As we know, the driving force of silicide reaction is the total reduction of system Gibbs free energy:

$$\Delta G_f = \Delta H_f - T \Delta S_f \tag{5.1}$$

respectively, at a given reaction temperature. Usually, the term $-T\Delta S_f$ is negligible compared to ΔH_f for solid-state reactions at low temperatures, and therefore the system free energy is largely determined by the enthalpy term [30]. In the silicide reaction between Ni and Si bulk or thin film, Si is considered unlimited, and the enthalpy of formation for each silicide reaction is listed in Table 5.1. It can be found that the Ni₂Si has the smallest formation enthalpy (-141 kJ/mol) and therefore the largest driving force to nucleate at a low reaction temperature, while NiSi2 has the largest formation enthalpy (-2 kJ/mol), and hence the NiSi₂ phase formation in thin film or bulk reactions is perceived as nucleation controlled, which can only occur at a temperature of above 750 °C. On the contrary, Ni is considered as an excess reservoir in the silicide reaction with NWs, and the enthalpy of formation for each silicide reactions is listed in Table 5.2. It's clear that several phases, including NiSi₂, Ni₂Si, and Ni₃₁Si₁₂, have small enough enthalpies that allow the formation of multiple phases simultaneously during the silicide reaction. This also indicates that nucleation is no longer the limiting step in determining the leading phase of NiSi₂, and kinetic competitive growth models suggest that the faster growth rate will separate the leading phase with the others [31]. At the same time, we should also consider the existence of θ -Ni₂Si phase, which is a high-temperature phase that is stable above 850 °C. In situ X-ray diffraction studies of NiSi substrate reaction show that θ -Ni₂Si is a transient phase, which may appear at low temperatures but is later consumed by δ -Ni₂Si phase with temperature increase [32], which is in agreement with the observations made on the reaction of Ni with Si NWs [26]. Another experiment to test the stability of θ -Ni₂Si phase suggests that high temperature formed θ -Ni₂Si phase transformed into δ -Ni₂Si and ε -Ni₃Si₂ during cooling down

Reactions	ΔH_f (kJ · mol ⁻¹)	$\Delta H_f (\text{kJ} \cdot \text{cm}^{-3})$	Molar volume (cm ³)
$2Ni + Si = Ni_2Si$	-141	-7.08	19.9
$3Ni_2Si + Si = 2Ni_3Si_2$	-15	-0.43	34.4
$Ni_3Si_2 + Si = 3NiSi$	-11	-0.75	14.6
$Ni_2Si + Si = 2NiSi$	-16	-1.09	14.6
$NiSi+Si = NiSi_2$	-2	-0.07	23.6

 Table 5.1 Enthalpy of formation for each silicide reaction with excess Si reservoir (thin film or bulk reactions)

Values adapted from Ref. [34]

Table 5.2 Enthalpy of formation for each silicide reactions with excess Ni reservoir (NW reactions)

Reactions	$\Delta H_f (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta H_f (\text{kJ} \cdot \text{cm}^{-3})$	Molar volume (cm ³)
$2Si + Ni = NiSi_2$	-88	-3.72	23.6
$NiSi_2 + Ni = 2NiSi$	-42	-2.90	14.6
$NiSi+Ni = Ni_2Si$	-55	-2.74	19.9
$Ni_2Si + 3Ni = 2Ni_2Si$	-97	-4.87	19.9
$12\mathrm{Ni}_2\mathrm{Si}+7\mathrm{Ni}=\mathrm{Ni}_{31}\mathrm{Si}_{12}$	-1819	-6.39	284.7

Values adapted from Refs. [21, 34]

below 825 °C, while on the other hand, that low temperature (460 °C) formed θ -Ni₂Si phases didn't decompose even during cooling down to room temperature [33]. These observations suggest that, although θ -Ni₂Si is a high-temperature stable phase, it also retains a certain type of stability at low temperatures, likely due to high kinetic barriers for phase transformation.

Many studies were carried out to control the phase formations in Si NW templates [27–29, 35–37]. These studies were driven with the desire to eliminate the Ni-rich silicide phases (e.g., $Ni_{31}Si_{12}$) that generally have higher resistivity which compromises the series resistance in NW transistors. A dielectric shell (SiO₂ [27, 35] or Al_2O_3 [29]) coating can exert a compressive stress to the silicide core and suppress the formation of phases that have high-volume expansion ratios. This is because high compressive stresses squeeze the interstitial sites through which Ni diffuses, increasing the activation barrier of Ni diffusion. As shown in Fig. 5.2a–d, an ALD Al_2O_3 layer with a thickness of 22 nm on a Si nanowire with a diameter of ~50 nm can effectively exclude Ni₃₁Si₁₂ phase in the formed nickel silicide sequence. Importantly, the leading silicide phase in direct contact with pristine Si determines the SBH and consequently charge injection/extraction, and therefore a better control of the leading phases could potentially fulfill various device functionalities. Since coexistence of multiple nickel silicide phases in NW is thermodynamically preferred, the leading phase adjustment relies on the kinetic competitions [28, 37]. It has been found that NiSi₂ growth rate is limited by interfacial reactions (the kinetic limiting steps will be revisited in Sect. 5.3) and remains constant at a given temperature despite the NW size. On the contrary, θ -Ni₂Si growth is diffusion limited and the



Fig. 5.2 Manipulation of nickel silicide phases in Si NW templates. (**a**) Schematic of reaction between Ni and Si NW with dielectric shell coating. (**b**–**d**) TEM images of nickel silicide growth in a Si NW with a thick (22 nm) Al₂O₃ shell at 800 °C for 30s. The leading phase is NiSi₂, and the Ni₃₁Si₁₂ phase with highest volume change is suppressed. (e) Schematic of reaction between Ni and Si NW with small diameter at high temperature. (**f**–**g**) TEM images of nickel silicide growth in a thin (33 nm) Si NW at 800 °C for 30s. The leading phase is θ -Ni₂Si in this case. (**h**) Schematic of reaction between Ni and Si NW with a thin Pt interlayer. (**i**–**j**) TEM image and elemental mapping of nickel silicide growth in a ~70 nm Si NW with 5 nm Pt interlayer and a thick Al₂O₃ shell, at 450 °C for 2.5 h. The leading phase and the only phase is NiSi. (TEM images are reproduced with permission from Refs. [28, 29]. Copyright 2012, 2013 American Chemical Society)

diffusion rate can significantly increase in Si NWs with smaller diameter. At a high reaction temperature, where stable θ -Ni₂Si phase is favored, there exists in principle a transition diameter, below which θ -Ni₂Si would be favored over NiSi₂ as the leading phase. Chen and et al. [28] derived this critical diameter of 234 nm, by extracting the diffusivity (D) of Ni in θ -Ni₂Si and the reaction constant (k) at NiSi₂/Si interface and setting the average growth rates of these two phases to be equal. Figure 5.2e–g demonstrates the feasibility of formation of θ -Ni₂Si as leading phase in a small (33 nm in diameter) Si NW at reaction temperature of 800 °C.

Thus far, the most preferred low-resistivity NiSi phase in bulk NiSi reaction was not yet observed in NiSi NW reaction and was only reported in point contact reaction in Si NWs [38, 39]. In order to manipulate the NiSi phase formation, Chen and et al. [29] inserted a very thin layer of Pt in between Ni pad and Si NW, schematically shown in Fig. 5.2h. Pt has a higher solubility in NiSi phase than that in NiSi₂ [40],

because the PtSi and NiSi share the same crystal structure with similar lattice constant and could potentially form solid solution [41]. Therefore, Pt promotes the NiSi phase formation rather than NiSi₂, and by combing the constraining dielectric shell (to suppress Ni-rich silicide phases), a single NiSi phase was experimentally observed as shown in Fig. 5.2i, j.

5.2.2 Metal-Germanide in Ge NWs

Benefiting from the intrinsically higher hole mobility, Ge NWs hold a great promise in PMOS devices, together with GeSi alloy [42] or Ge/Si core/shell [43] NWs. Similar to the case of Si, Ni is also the promising candidate for contact to p-type Ge, due to the small SBH and the ease of formation of Ni_xGe compounds. By virtue of being a group IV semiconductor, Ge has the same diamond lattice structure as Si, and many similarities exist between metal-germanide reactions and metal-silicide ones. In this section, we will review the different behaviors of metal-germanide phase formation in Ge NWs.

Firstly, no conclusive phase sequences have been observed in Ni reacting with Ge NWs over a broad reaction temperature range, and different Ni germanide phases have been reported at different reaction temperatures. Dellas et al. [44] carried out the solid-state reaction between a Ni pad and a Ge NW at the temperature range of 300~400 °C. The formed polycrystalline Ni_xGe phase (shown in Fig. 5.3a) was found to match Ni₂In prototype structure (hexagonal crystal structure) with the $P6_3/$ mmc space group. They pointed that the stoichiometry of Ni_xGe may deviate from x = 2 due to vacancies on one of the Ni sub-lattices [45], leading to similar lattice constants for several germanide phases (Ni₂Ge, Ni₅Ge₃, Ni₁₉Ge₁₂, Ni₁₇Ge₁₂, and Ni_3Ge_2 [46]. In comparison, their experimentally observed diffraction data was most consistent with Ni_3Ge_2 phase. They also reported that this germanide phase was independent of Ge NW growth orientations, and that further increase of reaction temperatures above 450 °C would lead to a decomposition and discontinuity in germanide segment, the reasons of which were not clear. Tang et al. [47] reported the Ni germanide reaction in <111> Ge NWs at the temperature range of 400~500 °C and observed a single crystalline orthorhombic Ni₂Ge phase (shown in Fig. 5.3b). They found an abrupt interface between Ni₂Ge and Ge NW, and the interfacial correlation was Ni₂Ge (100) || Ge $(1\overline{1}\overline{1})$ and Ni₂Ge $[0\overline{1}\overline{1}]$ || Ge $[01\overline{1}]$. At the reaction temperature of 650 °C, the same group reported cubic Ni₃Ge phase (shown in Fig. 5.3c) with same cubic structure to Ge [18]. Their observations have shown very similar lattice constant between Ni₃Ge and Ge with only $\sim 1.5\%$ lattice mismatch, which was different from the conventional lattice constant for cubic Ni3Ge phase [48, 49], as summarized in Table 5.3. Similar to Si NWs, oxide confinement was also found to suppress the formation of Ni-rich germanide that had large volume expansions. An Al₂O₃ shell coating led to the formation of



Fig. 5.3 Different Ni_xGe/Ge NW interfaces at different reaction temperatures. (**a**) Ni₃Ge₂ phase formed at 400 °C for 2 min anneal. Reprinted with permission from Ref [44]. Copyright 2010 American Institute of Physics. (**b**) Ni₂Ge phase formed at 500 °C for 60s anneal. (**c**) Ni₃Ge phase formed at 650 °C. (**d**) NiGe phase formation at 450 °C, with Al₂O₃ shell confinement. (**e**) Segregation of Ni_xGe nanoparticles upon thermal anneals. (**f**) Cross-sectional TEM of germanide nanowire coated with Al₂O₃ shell. There are segregated nanoparticles underneath the nanowire, the region that is not covered by Al₂O₃. (**g**) HRTEM image of the germanide phase in (**f**), which is NiGe. ((**b**–**g**) are reproduced with permission from Ref. [18]. Copyright 2011 Jianshi Tang et al.)

orthorhombic NiGe phase (shown in Fig. 5.3d) in adjacent to pristine Ge NW followed by Ni₂Ge phase, at reaction temperature of 450 $^{\circ}$ C.

Secondly, the nickel germanide reaction is usually accompanied with segregation of Ni_xGe nanoparticles. Tang et al. [18] found that the segregation of Ni_xGe nanoparticles could be caused by two factors, the instable native oxide, GeO_x, and the large lattice mismatch. As shown in Fig. 5.3e, with elongated reaction time Ni_xGe nanoparticles gradually formed at the surface of a germanide segment. When confined by the Al₂O₃ shell, Tang et al. have shown these segregated nanoparticles could be effectively suppressed, as shown in the NW cross section in Fig. 5.3f, except the bottom surface on substrate where the Al₂O₃ shell was not conformal. It's worth noting that the germanide phase here with an Al₂O₃ shell confinement was found to be NiGe as validated in Fig. 5.3g and had a large lattice mismatch of 77.7% with the Ge interface. This large lattice mismatch is another contributor to the formation of segregated nanoparticles at the non-coated surface. One possible way to eliminate the segregation is to introduce a Ni point contact on the Ge NW, benefiting from the smaller Ni flux through the limited contact area [18].

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-		Refs.		O [26, 28,	29]	0[29]		0[28]		O [26, 70]	O [26, 71]	O [72]		O [73]		O [74]			0 [44]	O [47]		O [18]	□[48, 49]	0[75]		0 [76]		(continued
		Interfacial plane structure		NiSi ₂ (111) Si (111)	NiSi ₂ [-110] Si [-110]	NiSi (-110) Si (1-11)	NiSi [001] II Si [110]	θ-Ni ₂ Si [110] Si [110]		1	1	PtSi (101) Si (111)	PtSi [010] Si [1–10]	CoSi ₂ (-111) Si (-111)	CoSi ₂ [110] Si [110]	MnSi(-2-14) Si(345)	MnSi [1-20] Si[3-1-1]		1	Ni ₂ Ge (100) Ge (1–1-1)	Ni ₂ Ge [0–11] Ge [01–1]	Ni ₃ Ge (111) Ge (111)	Ni ₃ Ge [110] Ge [110]	NiGe (001) Ge (1–1-1)	NiGe [010] Ge [01–1]	Cu ₃ Ge(211) Ge (1–11)	Cu ₃ Ge[-102] Ge [-112]	
	Volume	Change	1	0.99		1.21		1.54		1.65	1.99	1.49		0.96		1.18		1	1.55	1.57		?1.05	2.01	1.18		2.23		
		c (Å)	1	1		3.258		4.890		7.068	12.288	3.604		I		I		I	5.187	7.26		I		5.81		4.54		
	Istant	b (Å)	1	1		5.233		1		3.722	1	5.596		1		I		I	1	3.83		I		3.42		4.22		
	Lattice cor	a (Å)	5.431	5.406		5.659		3.805		5.004	6.671	5.935		5.365		4.556		5.658	3.95	5.11		?5.75	3.572	5.38		5.28		
-	Crystal	structure	Cubic	Cubic		Orthorhombic		Hexagonal		Orthorhombic	Hexagonal	Orthorhombic		Cubic		Cubic		Cubic	Hexagonal	Orthorhombic		Cubic		Orthorhombic		Orthorhombic		
, . , .		Reaction condition		300~650 °C		450 °C	Al ₂ O ₃ shell and Pt interlayer	800 °C	small radius	300~650 °C	300~650 °C	520 °C		800 °C		650 °C			300~400 °C	400~500 °C		650 °C		450 °C	Al ₂ O ₃ shell	310 °C		
		Phases	Si NW	NiSi ₂		NiSi		0-Ni ₂ Si		δ-Ni ₂ Si	Ni ₃₁ Si ₁₂	PtSi		CoSi ₂		MnSi		GeNW	Ni ₃ Ge ₂	Ni ₂ Ge		Ni ₃ Ge		NiGe		Cu ₃ Ge		

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		Crystal	Lattice cons	tant		Volume		
Phases	Reaction condition	structure	a (Å)	b (Å)	c (Å)	Change	Interfacial plane structure	Refs.
Mn ₅ Ge ₃	450 °C	Hexagonal	7.18	I	5.05	1.67	Mn ₅ Ge ₃ (0001) Ge(001)	0 [77]
							Mn ₅ Ge ₃ [-12-10] Ge [110]	
$In_xGa_{I-x}As$		Cubic	5.6533 + 0.4	405x				
Ni ₃ InAs	220~300 °C	1	1	1	1	I	Ni ₃ InAs(-1-10) InAs(-110)	0[55]
							Ni ₃ InAs[001] InAs [112]	
Ni ₃ InAs	High T	Orthorhombic	5.71	6.84	3.75	1.32	Ni ₃ InAs(001) InAs(001)	O [58]
	Theoretical						Ni ₃ InAs [110] InAs [100]	
Ni ₂ In _{0.53} Ga _{0.47} As	250~350 °C	Hexagonal	3.93	1	5.10	1.34	Ni ₂ In _{0.53} Ga _{0.47} As (0001)	0[67]
							$In_{0.53}Ga_{0.47}As$ (111)	
							Ni ₂ In _{0.53} Ga _{0.47} As [-12-10]	□[65, 66,
							$In_{0.53}Ga_{0.47}As$ [0–11]	68]
Ni ₂ GaAs	200~400 °C	Hexagonal	3.84	I	4.96	1.40	Ni ₂ GaAs (0001) GaAs (111)	□[60, 61]
							Ni ₂ GaAs [11–20] GaAs [1–10]	
Ni _x GaAs	200~400 °C	Hexagonal	3.79~3.90		5.01~5.07	1.38~1.48	1	[62-64]
$(x = 2 \sim 3)$								
Note: "O" represent	ts the studies carried or	at in NW channel	ls, while "□'	, represe	attents the studie	s on planar fil	ms	

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 Table 5.3 (continued)

5.2.3 Metal and III-V Compound Contacts

Continued progress in increasing transistor density incurs power dissipation constraints in MOSFET scaling [50], which may substantially elevate the packaging and cooling cost and make the chips impractical for most applications. One hasty way to lower the power consumption is to reduce the operation voltage, which would in return compromise the logic gate switching speeds [51]. A possible solution is to introduce a channel material in which the charge carriers travel faster than in conventional Si channels, allowing a lower operation voltage without sacrificing device performances. Therefore, III–V compound semiconductors, especially $In_xGa_{1-x}As$ ($0 \le x \le 1$), are regarded as potential replacement candidates due to their high electron mobility [19].

In order to take full advantages of the mobility enhancement, the contact requirements become very stringent for III–V transistors [52]. There are several general considerations for the metal contact to III–V transistors. Since more than two elements are involved in the solid-state reactions between contact metal(s) and III– V compound semiconductors, fundamental studies become more difficult in these multi-compound reactions. Simultaneously, a technical concern arises for the instability of the compound contact to III–V materials under elevated thermal processes [53], and therefore the electronic properties of compound contacts need to be carefully coordinated with the studies of their morphologies and phases. Despite the well-established contact theory in planar III–V channels [53, 54], only few detailed studies have been carried out on compound contacts in III–V nanostructures.

Chueh et al. [55] were the first to demonstrate the fabrication of Ni_xInAs compound contact in vapor-liquid-solid (VLS) grown InAs NWs, by reacting Ni pad with <110>-oriented InAs nanowires at 220~300 °C. The Ni_xInAs/InAs heterojunction showed an atomically abrupt interface, with the epitaxial relationship of Ni_xInAs $(\bar{1}\bar{1}0) \parallel InAs(\bar{1}\bar{1}0)$ and Ni_xInAs [001] $\parallel InAs$ [112]. Their EDS analysis gave a Ni:In:As atomic ratio of 58:22:20, suggesting the ternary phase as Ni₃InAs. Limited by the InAs NW growth orientation and the TEM viewing zone axes, details on the crystal structure and lattice constant of Ni₃InAs phase were not reported. In their following studies, a Ni:In:As atomic ratio of 49:25:26 was found in the reaction of Ni with planar InAs [56], and the Ni₂InAs stoichiometry was also found in NW channels [57].

Later, Schusteritsch et al. [58] presented a first-principle calculation for the composition of this Ni_xInAs compound contact. They used ab initio random structure searching (AIRSS) approach to determine the value of *x* and found that the Ni₃InAs phase has the lowest formation enthalpy among others ($x = 1 \sim 6$). For the different possible crystal structures of Ni₃InAs, their calculations showed that an orthorhombic structure with Pmmn space group gave the lowest formation energy, which was not observed in the limited experimental data [59]. The possible reason of the difference between first-principle simulation and experimental observations, as they also pointed out in the paper, can be intuitively concluded from our discussions



Fig. 5.4 Lattice structure of Ni_xGaAs. In principle, the stoichiometry can have a range of $x = 2 \sim 4$. The schematic shows Ni₂GaAs, and extra Ni atoms can occupy one or both of the " \star " sites to form Ni₃GaAs or Ni₄GaAs, respectively

in the Si NW Sect. 5.2.1 above, as the phase selection is not only determined by thermodynamics but also by kinetic competition, volume expansion, lattice mismatch, etc.

In fact, the stoichiometry has long been an argument in Ni_xGaAs compound contact to GaAs thin film structures [60–64]. Ni_xGaAs was observed as hexagonal lattice system, adopting NiAs (B8) crystal structure, with the value of *x* ranging in principle from 2 to 4 and the experimentally observed range to be within 2 to 3. As shown in Fig. 5.4, Ni atoms occupy the corner sites (0, 0, 0) and the edge sites (0, 0, 1/2), forming the hexagonal frame. Ga and As atoms occupy the (1/3, 2/3, 3/4) site and (2/3, 1/3, 1/4) site, respectively. There are still other two empty sites (1/3, 2/3, 1/4) and (2/3, 1/3, 3/4) that Ni can selectively occupy resulting in the possible stoichiometry of *x* from 2 to 4. Following experimental results presented in [65– 68], we will show that stoichiometry of x = 2 is the most commonly observed crystalline phase in In_{0.53}Ga_{0.47}As, as further squeezing of Ni in between the closely packed atoms becomes impractical.

We investigated the compound contact formation between Ni and $In_{0.53}Ga_{0.47}As$ NWs (the stoichiometry of $In_{0.53}Ga_{0.47}As$ originates from its epitaxial growth nature on InP substrate). These $In_{0.53}Ga_{0.47}As$ NWs are top-down etched from a 50 nm thin film, which has been pristinely transferred on insulator on Si substrate [67, 69]. There are several advantages of doing this: (i) top-down etched and horizontal lying NWs (or Fins) have more flexibility for the selection of size, length, and alignment to certain crystal orientations, and the fabrication approach is CMOS compatible; (ii) functional III–V transistors on Si substrate are always desired from a cost-effective aspect of industrial fabrication; (iii) studying the solid-state reactions



Fig. 5.5 Crystal structure analysis of nickelide phases. (a) Schematic illustration of the relative positions of FIB cut lamellas for panels b-c. HRTEM images of nickelide phase with FIB cut lamellas (c) along NW orientation and (b) perpendicular to the NW orientation. The nickelide phase was identified as Ni₂In_{0.53}Ga_{0.47}As with (0001) plane perpendicular to the NW orientation. Scale bars are 2 nm for all HRTEM images and 5 nm⁻¹ for all FFT images. (Reprinted with permission from Ref. [67]. Copyright 2015 American Chemical Society)

between metal and III–V on insulator can eliminate interfering influences and reactions with the III–V growth substrate. Details of the reaction between Ni and an $In_{0.53}Ga_{0.47}As$ [011] NW that has rectangular cross section are schematically shown in Fig. 5.5a. In order to identify the phase of Ni_xIn_{0.53}Ga_{0.47}As (referred to as "nickelide" for simplicity), focused ion beam (FIB) lamellas were prepared in two orientations as indicated by the red planes of Fig. 5.5a. From the corresponding TEM images in Fig. 5.5b, c, we extract the lattice constant of the nickelide structure and identify it as hexagonal Ni₂In_{0.53}Ga_{0.47}As phase through comparison to the known lattice values in the literature [65, 66]. This two-zone detection method eliminates possible errors in extracting the lattice constant associated with single-zone detection and provides an example to identify unknown phases with complicated compositions.

Unlike multiple silicide phases coexisting during the nickel silicide reaction in Si NWs, the nickelide segment in $In_{0.53}Ga_{0.47}As$ NW exhibited a single phase, $Ni_2In_{0.53}Ga_{0.47}As$, as shown in Fig. 5.6. Interestingly, the $Ni_2In_{0.53}Ga_{0.47}As$ crystal undergoes a gradual rotation from the reaction interface toward the Ni reservoir. The



Fig. 5.6 Cross-sectional TEM image of the entire nickelide region. The fast Fourier transform (FFT) patterns were collected from different regions along the NW. The nickelide (0001) plane is well aligned with $In_{0.53}Ga_{0.47}As$ (111) plane at the interface. But away from the interface, there is a gradual rotation of the crystal structure to maintain an equilibrium [0001] nickelide axis parallel to the NW [011] direction. Scale bar is 200 nm for the TEM image and 5 nm⁻¹ for all FFT patterns. (Reprinted with permission from Ref. [67]. Copyright 2015 American Chemical Society)

interface at the reaction front is Ni₂In_{0.53}Ga_{0.47}As (0001) || In_{0.53}Ga_{0.47}As (111) with the Ni₂In_{0.53}Ga_{0.47}As [0001] direction pointing 35.3° below the NW axis orientation of [011]. Far away from the interface, the Ni₂In_{0.53}Ga_{0.47}As [0001] direction is parallel to the [011] NW channel orientation. The crystal rotation of Ni₂In_{0.53}Ga_{0.47}As phase happens within about 200 nm near the Ni₂In_{0.53}Ga_{0.47}As/ In_{0.53}Ga_{0.47}As interface and undergoes a gradual change with defective crystallites (FFT pattern shows continuous arc for each diffraction spot rather than the paired sharp spots for twinned structures). Throughout the whole range of nickelide segment, the zone axes were fixed as $[\bar{1}2\bar{1}0]$, with Ni₂In_{0.53}Ga_{0.47}As $[\bar{1}2\bar{1}0] \parallel$ In_{0.53}Ga_{0.47}As (0011]. On the basis of these observations, we speculate that the nickelide phase growth starts with the energy preferred epitaxial planar interface of Ni₂In_{0.53}Ga_{0.47}As (0001) || In_{0.53}Ga_{0.47}As (111), and undergoes a post-growth crystal rotation to form the low-energy (10 $\bar{1}0$) top surface [67].

A closer look at the interfacial structure can be found in the HRTEM image in Fig. 5.7a. Here, we deduce that the nickelide phase growth follows layered steps from the top surface toward the bottom as indicated by the yellow arrows. This saw-tooth interface is believed to relax the strains at the growth interface. To better understand how Ni atoms fill into the lattice of $In_{0.53}Ga_{0.47}As$ and to briefly estimate the strain at the interface, we draw the atomic models for $In_{0.53}Ga_{0.47}As$ and $Ni_2In_{0.53}Ga_{0.47}As$ in Fig. 5.7b with their interfacial planes lying horizontally. In (or Ga) and As atoms have hexagonal arrangement inside the (111) planes, and upon $Ni_2In_{0.53}Ga_{0.47}As$ formation, Ni diffuses in between each In (or Ga) and As layers and breaks the bonds between these particular layers. Inside each layer, atoms remain in the hexagonal arrangement, and the atom-to-atom spacing decreases by



Fig. 5.7 TEM characterization and structural analysis of the Ni₄In_{0.53}Ga_{0.47}As/In_{0.53}Ga_{0.47}As interface. (**a**) HRTEM image at the nickelide (dark contrast) In_{0.53}Ga_{0.47}As (bright contrast) interface. The yellow arrows indicate the layered growth of nickelide on the interfacial plane of Ni₄In_{0.53}Ga_{0.47}As (0001) \parallel In_{0.53}Ga_{0.47}As (111) from top surface toward the bottom interface with HfO₂. (**b**) Atomic models of In_{0.53}Ga_{0.47}As and Ni₂In_{0.53}Ga_{0.47}As aligned along their [0001, 111] directions, respectively. The atomic models clearly indicate the nature of Ni squeezing in between each In (or Ga) and As layers. (Reproduced with permission from Ref. [67]. Copyright 2015 American Chemical Society)

~5.5% (according to their lattice constants summarized in Table 5.3). However, in the direction perpendicular to the interfacial plane, the layer-to-layer spacing of same atom increases by ~50.5%. Therefore, the In_{0.53}Ga_{0.47}As NW at the reaction interface experiences compressive stresses from both inside the interfacial plane due to lattice mismatch and perpendicular to the interfacial plane due to volume expansion in the reacted nickelide phase. The effect of strain on semiconductor energy bandedge structures is discussed in Sect. 5.4 of this chapter. Moreover, one could notice from the atomic models that further formation of Ni_xIn_{0.53}Ga_{0.47}As (x > 2) phases needs much higher energy for Ni to squeeze in between the closely packed III or V atoms inside each layer, and therefore a crystalline Ni₂In_{0.53}Ga_{0.47}As phase is observed over the entire reaction temperature of 250~350 °C. Higher reaction temperatures above 400 °C usually lead to deposition of the nickelide phase [63, 64].

5.3 Kinetics of the Solid-State Reaction Between Metal and Semiconductor NWs

The implementation of metal-semiconductor compounds as standard contacts to NW field-effect transistors (FETs) urges understanding and control over the dynamic processes in this metal-semiconductor solid-state reaction beyond the knowledge of phases discussed in Sect. 5.2. On one hand, the kinetics in NW reactions can be quite

different from that in thin film or bulk reactions, where the surface-to-volume ratio is tremendous. Size effects, defects, and stain effects can all play a role – or become dominant effects – in these nanoscale reactions. On the other hand, a well-controlled kinetic process is a prerequisite for realizing tunable channel lengths and ultimately ultrashort channel devices.

Ni is the dominant diffusion species in this silicide reaction, and there are generally two diffusion paths: through the entire NW cross section (volume diffusion) or through the few atomic layers at the surface of the NW (surface diffusion). Appenzeller et al. [78] were the first to discuss the kinetics of the NiSi NW reaction and to deduce the Ni diffusion path during the silicide formation process. They found a strong size effect on the silicide growth rate and plotted the silicide length (L_{silicide}) versus R^{-1} and R^{-2} . Based on their experimental observation that the $L_{\text{silicide}} \sim R^{-2}$ plot passed the origin point, they deduced a Ni volume diffusion dominant kinetics, with the assumption that the amount of diffused Ni (measured by the volume of reacted Ni silicide segment $L_{\text{silicide}} \cdot \pi R^2$) was constant and that the silicide length should approach zero for infinitely large NW ($R^{-2} \approx 0$) under a short reaction time. Later, Katsman et al. [79] argued that the extracted volume diffusion coefficient was much higher than realistic at the low reaction temperature of 280 °C. They replotted Appenzeller's data with $L_{\text{silicide}} \sim R^{-1/2}$ coordination following their own surface diffusion model and fitted the plot with linear approximation. This fitted line didn't pass through zero either, while they extrapolated this intercept as a transition diameter R_0 above which the interfacial diffusion (at silicide/Si interface) started to play a role.

Besides the Ni diffusion paths, there are also other limiting steps for the reaction kinetics. Lu et al. [38] studied the nickel silicide reaction in [111]-oriented Si NWs by point contact with Ni NWs. The silicide phase found in this study was nickelmono-silicide, NiSi, which exhibited a linear dependence of L_{silicide} with time, t, instead of the conventional $L_{\text{silicide}} \propto t^{1/2}$ dependence for a diffusion-dominant process. The authors ruled out the phase growth on the silicide/Si interface as the rate-limiting step, as their observed epitaxial growth rate was much faster than the diffusion speed. Therefore, they concluded that this point contact reaction was limited by the rate Ni dissolution into Si NW at the contact interface. Dellas et al. [80] investigated the silicide reaction at higher temperatures (400 \sim 500 °C) and found a NW orientation-dependent reaction kinetics. They attribute this effect to the differences in dominant phase formed in different NW growth directions, and [111]oriented (or [112]-oriented) NW had a linear $L_{\text{silicide}} \propto t$ (or hyperbolic $L_{\text{silicide}} \propto t^{1/2}$) kinetics due to the formed NiSi₂ phase (or θ -Ni₂Si phase). Chen et al. [28] extended the discussions on kinetics of different silicide phases and demonstrated the first phase selection by kinetic competition for small NWs at a high reaction temperature (800 °C) as discussed in Sect. 5.2.1.

All these debated aspects for the metal-semiconductor compound contact formation starve for a standard model that can quickly determine the rate-limiting steps



Fig. 5.8 A schematic illustration of the rate-limiting processes involved in nickelide formation in InGaAs NW channel. Due to volume expansion, the height of InGaAs NW increases from h to H after nickelide formation and the width increases from w to W. (Reprinted with permission from Ref. [67]. Copyright 2015 American Chemical Society)

and guide the extrapolation of relevant parameters. In this section, we propose a mono-compound phase model that depicts the kinetic steps involved in the metalsemiconductor reactions and provide a case study of nickelide reaction in InGaAs NWs. To the first order, stoichiometry does not influence the kinetics and is ignored here for simplicity. Then we will introduce the atomic-scale dynamics of the compound phase formation by utilizing in situ TEM technique and conclude with some specific cases when the kinetics may be altered.

5.3.1 Kinetics Modeling: A Case Study of Ni-InGaAs Reaction

This kinetic model extends previous modeling [17, 35, 81] of Ni silicide reaction in Si NWs that have cylindrical shape and focuses on more general cases in top-down etched and horizontally lying NWs that have rectangular cross sections. These top-down processed NWs (or Fin structures) present an ideal platform for studying compound metal contact formation with nanoscale channels at precisely defined widths and crystallographic orientations, in contrast to lesser control over such parameters in devices made on VLS-grown NWs that have been subject to similar studies. At the same time, we account for the volume expansion in the reacted segments, allowing for more accurate interpretation of experimental data.

As shown in Fig. 5.8, the mass transport of Ni atoms during the Ni-InGaAs compound (nickelide) growth involves three steps: (i) Ni dissolution across the Ni/nickelide interface, (ii) Ni diffusion along the formed nickelide segment, and

(iii) Ni-InGaAs reaction at the nickelide/InGaAs interface. The fluxes of Ni atoms in the above three processes can be expressed as:

$$F_1 = k_{\text{dissolve}} \left(C_{\text{Ni/Nickelide}}^{\text{eq}} - C_0 \right) \cdot (W + 2H) \cdot L_b$$
(5.2)

$$F_2 = -D_{\text{Ni}} \frac{C_L - C_0}{L_{\text{Nickelide}}} \cdot X \qquad X = \begin{cases} H \cdot W & \text{Volume Diffusion} \\ 2(H + W) \cdot \delta & \text{Surface Diffusion} \end{cases}$$
(5.3)

$$F_3 = k_{\text{growth}} \left(C_L - C_{\text{Nickelide/InGaAs}}^{\text{eq}} \right) \cdot hw$$
(5.4)

where k_{dissolve} and k_{growth} are the interfacial reaction rate constants for Ni dissolution into nickelide and for nickelide growth at the reaction front with InGaAs, respectively. At these two interfaces, $C_{\text{Ni/Nickelide}}^{\text{eq}}$ and $C_{\text{Nickelide/InGaAs}}^{\text{eq}}$ denote the equilibrium Ni concentrations. C_0 and C_L are the equilibrium Ni concentrations inside the formed nickelide segment, at zero-length position and at a reacted-length position, $L_{\text{Nickelide}}(t)$. The flux of Ni atoms diffusing along the formed nickelide segment, F_2 , depends not only on the diffusion coefficient of Ni species but also on the diffusion cross section X. The diffusion cross section describes the diffusion path of Ni atoms, with $H \cdot W$ for volume (bulk-like) diffusion and $2(H + W) \cdot \delta$ for surface diffusion, where δ is the thickness of high-diffusivity surface layer, taken conventionally to be one atomic layer high.

In steady-state, the fluxes of Ni atoms in the above three processes will reach the same value, $F_1 = F_2 = F_3 = F$, and F can then be derived as:

$$F = \frac{C_{\text{Ni/Nickelide}}^{\text{eq}} - C_{\text{Nickelide/InGaAs}}^{\text{eq}}}{\frac{1}{k_{\text{dissolve}} \cdot (W+2H) \cdot L_b} + \frac{L_{\text{Nickelide}}(t)}{D_{\text{Ni}} \cdot X} + \frac{1}{k_{\text{growth}} \cdot h_W}}$$
(5.5)

Here, we can find three terms in the denominator, each representing a ratelimiting mechanism. In order to solve this equation, the mass conservation of Ni atoms should be considered as follows:

$$HW \cdot \frac{dL_{\text{Nickelide}}(t)}{dt} = F \cdot \frac{M_{\text{Nickelide}}}{N_A \cdot \rho_{\text{Nickelide}}}$$
(5.6)

If we assume a constant, *P*, such that $P = M_{\text{Nickelide}} \cdot \left(C_{\text{Ni/Nickelide}}^{\text{eq}} - C_{\text{Nickelide/InGaAs}}^{\text{eq}}\right) / (N_A \cdot \rho_{\text{Nickelide}})$, and if we then substitute Eq. (5.6) into (5.5), we will get:

$$\frac{dL_{\text{Nickelide}}(t)}{dt} = \frac{P}{\frac{HW}{k_{\text{dissolve}} \cdot (W+2H) \cdot L_b} + \frac{HW \cdot L_{\text{Nickelide}}(t)}{D_{\text{Ni}} \cdot X} + \frac{HW}{k_{\text{growth}} \cdot hw}}$$
(5.7)

To solve this differential equation and to separate the three rate-limiting mechanisms, the terms in the denominator are considered one at a time.

If Ni supply is the rate-limiting step, then:

$$L_{\text{Nickelide}}(t) = k_{\text{dissolve}} \left(\frac{1}{H} + \frac{2}{W}\right) L_b P \cdot t$$
(5.8)

If Ni diffusion is the rate-limiting step, and Ni follows surface diffusion path, then:

$$L_{\text{Nickelide}}(t) = \sqrt{4PD_{Ni}\delta \cdot \left(\frac{1}{H} + \frac{1}{W}\right) \cdot t}$$
(5.9)

If Ni diffusion is the rate-limiting step, and Ni follows volume diffusion path, then:

$$L_{\text{Nickelide}}(t) = \sqrt{2PD_{Ni} \cdot t} \tag{5.10}$$

If interfacial reaction is the rate-limiting step, then:

$$L_{\text{Nickelide}}(t) = k_{\text{growth}} \frac{hw}{HW} P \cdot t$$
(5.11)

The conditions and properties of each rate-limiting step are summarized in Table 5.4. It can be clearly seen that for a diffusion-limited process, including surface diffusion and volume diffusion paths, the nickelide segment lengths have a hyperbolic dependence on time. However, for an interface-related limited process, including Ni dissolution at Ni/nickelide interface and nickelide growth at nickelide/ InGaAs interface, the nickelide segment lengths have a linear dependence on time. Among these four rate-limiting steps, the Ni source supply limit and the surface diffusion limit exhibit size dependence on NW dimensions. Even though Eq. (5.11) also involves geometric terms, the solution mainly relies on the expansion ratio in the cross-sectional area, indicating a dependence on the formed nickelide phase.

Table 5.4 Nickelide growth in InGaAs NWs for different rate-limiting steps according toEqs. (5.8, 5.9, 5.10 and 5.11)

		Size			
		depend	ence	Time deper	ndence
Rate-limiting step	Conditions	Yes	No	Linear (t)	Hyperbolic $(t^{1/2})$
Ni source supply limit	$k_{\rm dissolve} \ll k_{\rm growth}, D_{\rm Ni}$	\checkmark		1	
Surface diffusion limit	$D_{\rm Ni} \ll k_{\rm dissolve}, k_{\rm growth}$	\checkmark			\checkmark
Volume diffusion limit	$D_{\rm Ni} \ll k_{\rm dissolve}, k_{\rm growth}$		1		1
Interfacial reaction limit	$k_{\rm growth} \ll k_{\rm dissolve}, D_{\rm Ni}$		\checkmark	1	

Please note that this kinetic model considers a single-phase metallic compound formation during the metal-semiconductor reaction, and more complicated modeling with multiple-phase formations can be found elsewhere [82, 83].

From the experimental results of nickelide reaction in InGaAs NWs with different widths, clear size-dependent nickelide segment lengths are observed as shown in Fig. 5.9a, b. Ni diffuses into the InGaAs NW channels from both ends with the nickelide segment exhibiting a lighter contrast, and smaller NW channels have longer nickelide segment for the same annealing time. This indicates that either the Ni source supply limit or the surface diffusion limit is the rate-limiting step here in the nickelide formation in these top-down etched InGaAs NWs. The interface between nickelide and InGaAs is rougher in the <100>-oriented NWs, due to the crystalline correlation at interface as discussed in Sect. 5.2.3. The $L_{\text{Nickelide}} \sim t$ plots in Fig. 5.9c, d show hyperbolic curves with good $t^{1/2}$ fitting, suggesting a surface diffusion-limited process. Therefore, Eq. (5.9) is used to describe this kinetic process, and the data is replotted as $L_{\text{Nickelide}} \sim \sqrt{1/H + 1/W}$ in Fig. 5.9e, f. As the volume expansion is found to mainly cause the height change in these experiments and negligible width change is observed, the w is used here to replace W. For both orientations, linear fits with two slopes agree well with data measured for each annealing time. The different slopes become more eminent as the annealing time is larger than 25 min. The "corner" points (deflection points in linear fits) correspond to NW widths of ~ 100 nm for <110>-oriented NWs and ~ 150 nm for <100>-oriented NWs.

These deflection points indicate certain changes are happening with the increase in NW size. The insets in Fig. 5.9c, d also show an incubation time before measurable nickelide lengths for NW channels were detected, and the incubation time increases as the NW width becomes larger. However, there's no incubation time for the planar films, indicating different kinetic processes between thin film structures and NW channels. Indeed, metal diffusion in thin films is always considered as volume diffusion, while we have demonstrated the surface diffusion dominant behaviors in NW reactions. The incubation time is likely associated with Ni diffusion through the body of the InGaAs NW underneath the Ni pads, where the larger NWs require longer time for Ni to fill the entire NW cross section. At the same time, larger NWs have much smaller surface-to-volume ratio, which may be attributed to some contribution from volume diffusion instead of pure surface diffusion, causing the deflections in the linear fittings in Fig. 5.9e, f.

To further clarify this, the length of nickelide segment is plotted against both the time and geometry factors in Fig. 5.10a, b. Accounting for both geometric and time dependencies, all experimentally measured data for different annealing times and at a single temperature can be linearly fitted (in agreement with Eq. 5.9) validating the surface diffusion dominant kinetic process. The non-zero intercept with the x-axis indicates an average incubation behavior of all NWs with 250 °C thermal treatment, but no average incubation time for higher temperature treatments. However, larger



Fig. 5.9 Size, orientation, and time dependence of nickelide formation. (**a** and **b**) SEM images illustrating the size-dependent and orientation-dependent morphologies for nickelide contacts with InGaAs fin channels pre-defined in <110> and < 100> orientations, respectively. Scale bars are 5 μ m. (**c** and **d**) The length of nickelide segments versus annealing time at 250 °C for <110> and < 100> fin orientations, respectively. In both orientations, the data were well fitted with a $t^{1/2}$ dependency. (**e** and **f**) The length of nickelide segments versus $\sqrt{1/w + 1/H}$ at 250 °C with two different fin orientations, <110> and < 100>, respectively. (Reproduced with permission from Ref. [67]. Copyright 2015 American Chemical Society)



Fig. 5.10 (a and b) Combined plots of nickelide segment length in relation to annealing time and NW geometrical factors, according to the surface diffusion-limited model, at three different growth temperatures and with NW orientations of <110> and <100>, respectively. (c-f) Extracted kinetic parameters for NW channels and planar films in both <110> and <100> orientations. (Reproduced with permission from Ref. [67]. Copyright 2015 American Chemical Society)

NWs (left-side data points of each data set, color-labeled) fell below the linear trend, indicating a deviation from the surface diffusion-limited kinetic model. Interestingly, these deflected data points gradually extend approaching the black squares, which are the data points obtained from nickelide growth in InGaAs thin films. All those observations suggest that the behaviors of nickelide formation in larger NWs gradually deviate from surface-dominant to a volume-dominant diffusion-limited growth process. Then, the diffusion coefficients can be extracted and plotted according to the Arrhenius relationship, $D \propto e^{-E_a/kT}$, followed by the extrapolation of activation energies of nickelide formation in both NW channels and film structures.

The above analysis provides a general way of investigating the kinetic processes during the metal-semiconductor reactions, and NWs with cylindrical shape can be derived similarly by replacing the geometry factors with those related to the NW diameter, R [17].

5.3.2 Atomic-Scale Dynamics

The dynamic process during metal-semiconductor reaction is reflected by the ledge nucleation and movement at atomic scale. Generally, a ledge or a train of ledges form on the compound contact/semiconductor interface and propagate through the entire cross section of NWs. In situ heating TEM technique provides the platform to observe these ledge (or called step) events with atomic resolutions [84].

In the study of CoSi₂ formation in Si NWs, Chou et al. [73] prepared the [111]oriented Si NWs with point contact of Co NWs and annealed the sample inside TEM chamber at 800 °C with real-time video recordings. They observed repeating events of the nucleation and stepwise growth mode during the epitaxial CoSi₂ phase formation, which has the same crystal structure and close lattice constant with pristine Si as seen in Table 5.3. Shown in Fig. 5.11a-d are the HRTEM images near Si/CoSi₂ interface, with the step movements labeled on the figures. By recording these repeating nucleation and growth events, they plotted the CoSi₂ atomic layers as a function of time in Fig. 5.11e, and several information can be interpreted from this plot. First, the vertical lines in this plot represent the steps of newly formed CoSi₂, and the height of each vertical transition is constantly that of one atomic layer of $CoSi_2$ (111) plane, indicating the layer-by-layer growth nature of $CoSi_2$ phase. Second, these vertical lines are not perfectly in parallel with y-axis but are sloped with a certain width that corresponds to the growth time of each CoSi2 atomic layer with the average value of ~ 0.17 s. Third, the horizontal segment in between vertical lines is the stagnation period before the nucleation of another step, which is called incubation time of nucleating a step. Taking into account the incubation time for nucleating every step, the average growth rate of $CoSi_2$ along the axial direction is 0.0365 nm/s. The radial growth rate (step velocity) is about 135 nm/s, calculated by the average step growth time and NW diameter, which is about 3700 times faster than the axial growth rate. This also indicates that interfacial reaction was not the rate-limiting step in this cobalt silicide growth. Fourth, the stair-step plot in Fig. 5.11e can be treated as the microcosmic view of a conventional $L_{\text{silicide}} \sim t$ relationship (discussed in Sect. 5.3.1), in which a linear dependence was found over a long reaction time. The authors attribute this linear time dependence to a Co source supply limited reaction, which agrees with our judgment in Table 5.4. Moreover, each step of CoSi2 showed a homogeneous nucleation behavior in the center of Si NW atop the CoSi₂/Si interface instead of the heterogeneous nucleation at the triple point of oxide shell, Si, and $CoSi_2$. Though homogeneous nucleation was seldom expected in theory, the authors explained the nucleation behavior here that the energy of oxide/silicide interface is higher than that of oxide/Si interface reducing the nucleation frequency at the triple points. They provided further experimental evidence [39] in Fig. 5.12a, b that the steps slowed down as approaching the oxide/Si/CoSi₂ triple points due to the high energy barrier. Their in situ TEM study of Ni point-contacted Si NW showed similar homogeneous nucleation of steps, as shown in Fig. 5.12c, d.



Fig. 5.11 (**a**-**d**) In situ HRTEM image sequences of growing CoSi₂/Si epitaxial interfaces within a [111]-oriented Si NW. (**e**) Plot of CoSi₂ atomic layers as a function of time to show the nucleation time and growth time of each step. (Reproduced with permission from Ref. [73]. Copyright 2008 American Chemical Society)

5.3.3 Modified Kinetic Process

Through the discussions above on kinetics of the solid-state reactions between metal and pristine semiconductor NWs, we mentioned several factors that potentially dominated the rate-limiting steps, such as NW sizes, surface oxide, reaction temperature, and formed phases. A table (Table 5.5) can be found at the end of this section that summarizes the reaction kinetics and extrapolated rate constants in metal-semiconductor compound formation in NW channels. In the following paragraphs,



Fig. 5.12 (a and b) HRTEM image and schematics of the CoSi₂/Si epitaxial interfaces at the oxide/ Si/CoSi₂ triple point. (c and d) In situ HRTEM image sequences of growing NiSi/Si epitaxial interfaces within a [111]-oriented Si NW. (Reproduced with permission from Ref. [39]. Copyright 2009 American Chemical Society)

we will discuss another important factor that may modify the nucleation and growth behaviors of compound contact in NW channels: defects.

In advanced semiconductor technology nodes, defects are intentionally built into the device to tailor the stress in Si channel. The stress memorization technology [85] is one example that utilizes stacking faults to exert tensile strain in the channel by inducing missing planes in the source/drain regions. In other instances, defects can be unintentionally introduced to the S/D regions during dopant implantation and subsequent activation thermal anneal [86]. Therefore, understanding the interactions between metal-semiconductor reactions and defects becomes important in controlling compound contact formation in defect-engineered nanochannels.

We previously investigated the nickelide silicide nucleation and growth in the presence of defects in Si NWs [87]. The Si NWs are grown at different conditions [88], to intentionally introduce two types of defects: (1) twin boundary (TB) along the axial direction of the NW with a high growth pressure and (2) Si nanoparticles on the NW surface forming the grain boundary (GB) with high growth temperature. It has been found that the NiSi₂ prefers the heterogeneous nucleation at the defect sites in order annihilate the high-energy interfaces.

As shown in Fig. 5.13, the NiSi₂ phase grows on the Si (111) plane in a layer-bylayer manner, and the growth fronts move asynchronously at two sides of the TB. The steps nucleate at the TB but never propagate across it, because the high energy barrier of forming new NiSi₂/NiSi₂ TB prevents so. The lagging interface can catch up with the leading interface because the NiSi₂/Si corner at TB is a preferable hetero-nucleation site, so on the average asynchronous step height does not grow

	Refs.	80			[35]				[81]		[28]				[18]	[55]		[67]				[89]	
	Rate constant	1			Without shell	$D \sim 3.6e^{-12} \text{ cm}^2/\text{s}$	With shell	$D \sim 9.6e^{-13} \text{ cm}^2/\text{s}$	1		$k = 1.2e^{-5} \text{ cm}^2/\text{s}$ (I)		$D = 2.3e^{-10} \text{ cm}^2/\text{s}$ (II)	$D = 3.65e^{-10} \text{ cm}^2/\text{s}$	1	$D = 1.13e^{-10} \text{ cm}^2/\text{s}$	(280 °C)	$D_{110} = 1.33e^{-10} \mathrm{cm^2/s}$	$D_{100} = 1.08e^{-10} \mathrm{cm^2/s}$	(30 nm, 300 °C)		1	
pound contacts	Rate-limiting step	Interfacial reaction	Surface diffusion		Surface diffusion				Source supply $(I) \rightarrow diffusion$	(II)	Interfacial reaction (I) \rightarrow diffu-	sion (II)	Diffusion		Linear t dependence	Volume diffusion (size	independent)	surface (small r) \rightarrow	volume (large r) diffusion			linear t dependence	
l semiconductor NW form con	Activation energy (eV/atom)	0.76 ± 0.10	1.45 ± 0.07		1				1.7 ± 0.15		1.79 ± 0.10 (I)		1.64 ± 0.24 (II)	I	0.55 ± 0.05	~ 1.04		~1.14 (surf, [110])	~1.12 (surf, [100])	~1.25 (vol, [110])	~1.23 (vol, [100])	0.66~1.60	(different interface
cs when metal and	Temperature range	400~550 °C			300~440 °C				300~440 °C		300~800 °C		800 °C		400~500 °C	220~280 °C		250~300 °C				264~354 °C	
ary of reaction kineti	Phase	NiSi ₂	0-Ni ₂ Si		NiSi ₂				Ni _x Si		NiSi ₂		⊒-Ni ₂ Si		Ni ₂ Ge	Ni ₃ InAs		Ni ₂ In _{0.53} Ga _{0.47} As				Au _x GaAs	(no-epi)
Table 5.5 Summ	Nanowire	Si [111]	Si [112]	(50~75 nm)	Si in SiO ₂ shell			(10~100 nm)	Si	(25~50 nm)	Si [111]		(20~234 nm)		Ge [111]	InAs [110]	(20~40 nm)	$In_{0.53}Ga_{0.47}As$	[110] and [100]	(30~500 nm)		GaAs [111]	(<100 nm)

or NW form ÷ pure ato 2 5 ction kinetics wh f Curry C

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Fig. 5.13 (**a** and **b**) NiSi₂ growth in Si NW with a TB. (**c**–**f**) and (**g**–**j**) HRTEM sequences showing the nucleation and propagation of NiSi₂ steps at the leading interface and at the lagging interface, respectively. Scale bar is 10 nm for (**a**) and 3 nm for all the rests. (Reprinted with permission from Ref. [87]. Copyright 2013 American Chemical Society)



Fig. 5.14 (a) NiSi₂ growth in Si NW with TB running along its central axis and GBs present at its surface. (b) Zoom-in HRTEM image of a cluster of surface grains. (c-f) and (g-j) HRTEM sequences showing the nucleation and propagation of NiSi₂ steps at the leading interface and at the lagging interface, respectively. Scale bar is 10 nm for (a) and 3 nm for all the rests. (Reprinted with permission from Ref. [87]. Copyright 2013 American Chemical Society)

significantly, given that Ni supply is equally available for both halves of the bi-crystal. With the presence of GBs on the NW surface as shown in Fig. 5.14, the heterogeneous nucleation is further facilitated and the steps are found to start from the GB and propagate toward the TB, in both leading and lagging interfaces, indicating that the GB is the more energetically preferred nucleation site.

These observations are related to the effectiveness of nucleation barrier reductions in $NiSi_2$ phase formation, and this reduction can be evaluated at the three



Fig. 5.15 (a) Schematic of three different heterogeneous nucleation sites. (b) Zoom-in view of the heterogeneous nucleus with disk shape and the correlation between different surface energies and contact angle θ . (c) Reduction in the nucleation barrier at different heterogeneous sites. (Reprinted with permission from Ref. [87]. Copyright 2013 American Chemical Society)

possible heterogeneous nucleation sites (illustrated in Fig. 5.15a): (1) TB, (2) "corner," and (3) surface GB, by calculating [87]:

$$\frac{\Delta G_{\text{hetero}}^*}{\Delta G_{\text{homo}}^*} = \frac{(\pi - \theta) + \sin \theta \cos \theta}{\pi}$$
(5.12)

where $\Delta G_{\text{hetero}}^*$ and ΔG_{homo}^* are the heterogeneous and homogeneous nucleation barriers, respectively. The contact angle θ is given by Young's equation, $\overline{\gamma} \cos \theta + \gamma_{\text{defect}} = \gamma_{\text{new}}$, in which $\overline{\gamma}$, γ_{defect} , and γ_{new} are the different interfacial energies as shown together with θ in Fig. 5.15b. In the three different nucleation sites, the energies for original defect γ_{defect} and new interface γ_{new} have different values, which are summarized in reference [87]. Using these values, the nucleation barrier reductions can be plotted in Fig. 5.15c, as a function of $\overline{\gamma}$. Therefore, with a reasonable estimation of $\overline{\gamma} = 1.2\gamma_{\text{NSi}_2}^{\text{epi}}$, the values of $\Delta G_{\text{hetero}}^*/\Delta G_{\text{homo}}^*$ can be calculated for TB, "corner," and GB as 0.93, 0.90, and 0.83, respectively. This indeed proves that the nucleation is more preferred on GB than "corner" and than TB sites.

5.4 Electrical Properties

Thus far, we discussed the phases of the metal-semiconductor compound contacts and the kinetics during the solid-state reaction processes, but the end goal of these metallurgical studies is to achieve a robust control over the electrical properties of the compound contacts and the resulting NW FET performances. It has been found that the S/D series resistance increasingly becomes the limiting factor for integrating nanostructures into high-performance electronics and the dominant performance degradation component below 10 nm node [90]. Therefore, understanding the electrical properties of the nanoscale electrical contacts, especially compound contacts, is a key step for fulfilling the leap from laboratory to real-world technology [91].

Here we will start by introducing the various applications of most commonly used compound contacts and continue with contact theories to NW channels and reports on the ultrashort channel devices. We summarize the property of compound contacts and the performance of NW FET devices discussed in this section in Table 5.6.

5.4.1 Electrical Applications of Compound Contacts

Nickel silicide and nickel germanide are most commonly used contacts in conventional CMOS technologies and extend their wide applications to NW FET studies. NiSi has low annealing temperature, low resistivity, and superior scaling to linewidths <100 nm [22]. Planar-geometry NiSi-based contact demonstrated a specific contact resistance of $<10^{-8} \Omega \text{cm}^2$ [24]. Its low density, smoother interfaces with Si, and less Si assumption add up to a superior contact to ultrathin Si-oninsulator device layer [23]. The planar-geometry NiSi has a Schottky barrier height (SBH) of 0.75 eV to n-Si and 0.39 eV for p-Si at room temperature [14], and the silicide work functions can be further adjusted by varying the doping concentrations in Si before silicide formation [92]. In Si NWs, NiSi₂ is the most commonly observed first phase interfacing with pristine Si.^{13,15,16} There are usually two types of coherent NiSi₂/Si interfaces: type A interface, where NiSi₂ has the same orientation with Si, and type B interface, where NiSi₂ forms a twin boundary-like interface. It has been found that type A NiSi₂/Si interface has an electron SBH (0.64 eV) that is 0.14 eV smaller than that of a type B interface (0.78 eV) [93].

Nickelide compound was also demonstrated to be a superior contact to planar III– V channels, such as $In_xGa_{1-x}As$ (referred in short as InGaAs). First, this Ni-InGaAs compound forms at a low annealing temperature, meeting a good thermal processing

		Dafe	Kers.	[11]		[117]		[26]	[118]			[02]		[72]		[101]	[47]		[75]				[119]
		I_{\max}	Imin	Ι		10^{7}		$\sim 10^{3}$	1			1		>10 ⁷		10 ⁵	>10 ³		10^{5}				>10 ⁵
	device	Mobility (cm ² /V/	s)	325 (h)		– (i)		1	1			1		168 (h)		1	65.4 (h)		210 (h)				730 (h)
	punodu	8m ((crf)	0.275		I		~15	I			I		~12		I	0.013		0.168				б
	onductor/cor	SS ⁻¹	(III V/dec)	I		I		350	I			I		110~220 (h)	320(e)	~180	I		2330				100
ç	nd/semic	$-V_{ds}$	()	1		1		0.01	1			1		0.2~1		1.2	0.1		0.1				0.01
דד מראורר	Compour	$R_C \over (\Omega - \mathrm{cm}^2)$	_	I		$\sim 10^{-6}$		I	I			I		I		I	I		I				I
		Gate	alelecuric	Back:	600 nm SiO_2	Back:	300 nm SiO_2	Top: 10 nm HfO ₂	1			1		Top: 7 nm HfO ₂		BOX	Back:	330 nm SiO_2	Back:	330 nm SiO_2	(Al ₂ O ₃	passivation)	Top: 4 nm HfO ₂
r puttott		L L	(IIIII)	e		0.67		0.017	1			1		2.3		0.5	3		0.67				0.19
רוא מווח חו	Channel	d (mm)	(IIIII)	30		20		32	1			1		50		8	40		70				18
יום ביווומ		SBH	(cv)	I		I		I	I			I		~0.2		~0.3 (n)	~0.2		0.11				I
y or compour	l contact	J _{max}	(A/CIII)	>10 ⁸		I		I	1.6×10^{8}	1.2×10^8	8×10^7	>10 ⁸		>10 ⁸		I	$3.5 imes 10^7$		I				I
וויר הו ההריו	Compound	(uno On)	(mo-22m)	10		I		I	13 ± 2	25 ± 1	60 ± 2	21		28.6		I	88		I				I
ייש א שווווומ		(J.)T	1(-1)	550		470		400	500	(poly-Si	(MN)	850	(CVT)	520		450	400		450				300
ד מוחב היה ב		Dhaca	rnase	NiSi		Ni _x Si		$NiSi_2$	NiSi	Ni ₂ Si	Ni ₃₁ Si ₁₂	Ni ₂ Si		PtSi		ErSi _{2-x}	Ni2Ge		NiGe				NiSi _x Ge _y

Table 5.6 Summary of the property of compound contacts and the performance of NW FET devices

$NiSi_xGe_y$	300	1	I	I	18	0.07	Top: 4 nm	I	0.5	~ 200	78	136 (h)	10^{5}	[120]
						0.04	HfO_2			~290	91	91 (h)		
Ni_2Ge	300	I	1	I	30	0.4	Top: 10 nm	$\sim 10^{-8}$	0.1	260	1.1	50 (h)	10^{5}	[114]
Ni ₂ Ge/ NiSi					20	0.3	HfO_2			140	4	200 (h)	106	
Cu ₃ Ge	310	34	$5 imes 10^7$	0.218	20~30	0.7	Back:	1	0.2	1	I	264 (h)	>10 ³	[]20
							200 mm 2102							
Cu ₃ Ge	250	I	1	0.115	35	0.25	Top: 20 nm	I	0.2	830	I	142 (h)	>10 ³	[121]
				(Ga			SiO_2							
				+										
Mn ₅ Ge ₃	450	240	1	0.25	50	0.5	Back:	1	0.1	I	0.25	>170 (h)	10 ⁵	[12]
							$300 \mathrm{nm}\mathrm{SiO_2}$							
							(Al ₂ O ₃							
							passivation)							
Ni ₃ InAs	250	167	10^{8}	0>	~30	0.28	Buried:	I	0.5	I	I	I	10^{5}	[55]
				(<i>u</i>)			60 nm LTO							
ρ here is the	resistivity	of pure con	npound phase	as NW s	hape. SB	H is the	hole Schottky b	arrier heig	ht excep	t for ErSi _{2-x}	and III-	V NWs. SS ⁻	¹ is the	inverse
subthreshold	d slope		•		4		•	,						

budget. It has been reported that nickelide starts to form at around 230 °C, and the formed phase is thermally stable between 350 °C and 450 °C [94]. Unlike the phase transition of nickel silicide at elevated temperatures, Ni-InGaAs suffers a degradation of electrical properties at 450 °C and above, resulting from the decomposition of the quaternary compound to binary compounds. Second, atomic abrupt interfaces were found in between the nickelide contact with III-V NW channels [55, 67], enabling an accurate control of the channel lengths. Third, selective etching of excessive Ni from nickelide contact with concentrated HCl facilitates the selfaligned gate process [95]. Most importantly, the Ni-InGaAs alloy has a low sheet resistance (20–25 Ω /square) [96, 97] and a low electron SBH. Ivana et al. [98] observed the alignment of nickelide contact to near conduction band of $In_{0.53}Ga_{0.47}As$ at interface by using ultraviolet photoelectron spectroscopy, which gave a hole SBH of 0.8 ± 0.1 eV and an ohmic contact to n-In_{0.53}Ga_{0.47}As. Mehari et al [99] obtained an electron SBH of 0.2396 \pm 0.01 eV for n-In_{0.53}Ga_{0.47}As through temperature-dependent current-voltage characteristics. These different values may originate from different interfacial properties between nickelide contact and InGaAs channel, which requires detailed studies on SBH of nickelide contacts in NW channels. Generally, a good ohmic contact is readily formed between nickelide contact and $In_xGa_{1-x}As$ that has high "In" content (x > 0.7), due to the Fermi-level pinning at the contact interface [100]. Currently, electrical studies on nickelide contacts to III–V NWs are still lacking [55].

Besides the Ni-based compound contacts, other metals have also been investigated in the solid-state reaction with semiconductors to form contacts, demonstrating a wide variety of applications. Erbium silicide, $ErSi_{2,x}$, was used to contact with n-type top-down etched Si NW, and a low electron SBH of ~0.3 eV was reported [101]. Platinum silicide, PtSi, that formed in the SiNW has a low hole SBH of ~0.2 eV, with a minimum achieved channel length of 8 nm [72]. At the same time, many compound contacts exhibit good magnetic properties, allowing the study of spin-polarized carriers in semiconductor NWs. Unusual ferromagnetic properties in single-crystalline CoSi NW were observed, significantly different from the diamagnetic properties in CoSi bulk [102]. Single crystal MnSi NW had paramagnetic to ferromagnetic transition temperature of 29.7 K, and the MnSi/p-Si/MnSi NW transistor was employed to study the carrier tunneling via the Schottky barrier and spin-polarized carrier transport in the Si NW [74]. Paramagnetic FeSi NW was transferred into Fe₃Si NW by a diffusion-driven crystal structure transformation method, with the Fe₃Si NW showing high-temperature ferromagnetic properties with $T_c \gg 370$ K [103]. In Ge NW system, there are also analogous ferromagnetic compound contacts, such as Fe₃Ge [104], Ni₃Ge [104], Mn₅Ge₃ [77, 105], etc., to investigate the electrical spin injections and detections in Ge NW transistors.

Moreover, asymmetric metal-semiconductor compound contacts can also be introduced to NW channels to expand their electrical functionalities. One approach is to form two different metal silicide at the opposite ends of the Si NW. Wu et al [106] reported the fabrication of β -Pt₂Si/ β -Ni₂Si, β -Pt₂Si/ θ -Ni₂Si, and β -Pt₂Si/



Fig. 5.16 (a) Schematic of nickel/platinum dual silicide formation in a Si NW. (b) Low magnification and (c) high magnification TEM images of the β -Pt₂Si/ θ -Ni₂Si interface. (d) Schematic of the ternary compound formation at the interface with further interdiffusion. (e) Schematics of the infrared light-sensing mechanism and the time-dependent photoresponse with 940 nm infrared light turned on and off repeatedly. (Reprinted with permission from Ref. [106]. Copyright 2016 American Chemical Society)

Ni_xPt_{2-x}Si/Pt_xNi_{2-x}Si/ θ -Ni₂Si axial heterostructures by depositing Pt and Ni on two sides of the Si NW and consequent annealing at 650 °C for certain controlled times. Shown in Fig. 5.16a–c are the schematics of the dual silicide formation and the TEM images of the merged interface between β -Pt₂Si and θ -Ni₂Si. Further annealing led to the intermixing of binary compounds to ternary compounds at the interface, as shown in Fig. 5.16d. Though Pt₂Si/Ni₂Si NW gave the lowest resistivity of 593.3 μ Ω cm, the Pt, Ni, and Si ternary NW heterostructures exhibited an excellent infrared light-sensing property, owing to the excitation of trapped carriers in the defective ternary compound region (shown in Fig. 5.16e).

In another approach, the asymmetric compound contacts can be formed in Si-Ge axial NWs with the same-metal reactions at the opposite ends. This offers a unique opportunity for exploring nanochannel devices with asymmetric contacts to assist charge transport in one desired direction and block it in the opposite direction. An example is shown in Fig. 5.17, in which Ni was used to contact the both ends of a Si-Ge axial NW [107]. In such a device, the difference in barrier heights at either end of the channel can add to the total potential drop in the channel and enhance current



Fig. 5.17 (a) Schematic of the Si-Ge asymmetry SBH FET device, and the Silvaco simulated energy band-edge diagrams in on-state. Dashed lines correspond to the situation of a pure Si channel under the same bias conditions. (b) Transfer curve of a p⁺ Ge–Si NW heterostructure SBFET showing $10^7 I_{on}/I_{off}$ ratio ($V_{SD} = 1$ V). Inset is an SEM image indicates the S/G spacing of ~40 nm, G length of ~200 nm, and G/D spacing ~260 nm. Reproduced with permission from Ref [107]. Copyright 2011 American Institute of Physics

transport in one direction. The potential drop across the valence band edge along the channel with applied S/D voltage can be expressed as:

$$|E_{\nu(S)} - E_{\nu(D)}|/q = V_{SD} + \Delta E_{\nu(Ge-Si)}/q + \varphi_{Bp(S)} - \varphi_{Bp(D)}$$
(5.13)

where V_{SD} is the applied source and drain voltage and $\Delta E_{v(Ge - Si)}$ is the average valence band offset between Si and Ge with the value ~0.57 eV. $\varphi_{Bp(S)}$ and $\varphi_{Bp(D)}$ are the hole SBH at the source and drain sides, respectively. The built-in potential drop in this asymmetry-contact transistor, $\Delta E_{v(Ge - Si)}/q + \varphi_{Bp(S)} - \varphi_{Bp(D)}$, can be as large as 0.82 V and can therefore significantly accelerate the hole transport from the Si to the Ge side. This resulted in an excellent I_{SD} modulation with on/off ratio of 10⁷ exceeding NW FETs made on pure p⁺ Ge or Si segments. This device architecture adds an important ability to accommodate band offsets and built-in electric fields in the conduction or valence bands utilizing asymmetry SBH at S/D of NW FETs. By proper selection of metal-semiconductor barrier heights, the functionalities can be thus be expanded for next-generation semiconductor devices.

5.4.2 Band Alignment and Charge Injection

The charge injection from metal-compound contacts into semiconductors is largely dominated by the band alignment at the contact-semiconductor interface. Due to the different contact geometries and size effects, NW transistors exhibit distinct band alignment and charge injection properties than their bulk counterparts [91]. Here, we will discuss several theoretical studies of the nanoscale contacts.



Fig. 5.18 Schematics for the band alignment diagrams for (a and d) planar-geometry contact, (b and e) end-bonded contact, and (c and f) side contact

For planar-geometry contacts (Fig. 5.18a), metal is deposited on the semiconductor surface followed by thermal anneal to form the compound interfacial layer. For nanoscale contacts, there are generally two categories: end-bonded contacts and side contacts [91]. The end-bonded contact (Fig. 5.18b) refers to the case that the metal or metallic contact has an abrupt interface with semiconductor in axial direction of nanochannels, in which atomic bonds form between the contact and the semiconductor. The compound formations in NW channels through metal diffusions as we discussed above all belong to this category. The side contact (Fig. 5.18c) refers to the metal embedded geometry in the NW radial direction. A simple deposition of metals on top of the NW is considered as in this category, in which a weak bond forms in between metal and NW. It has also been found that a metal that reacts with semiconductor at high temperature can readily form a thin layer of metal-semiconductor compound at the surface of NW upon deposition at room temperature, due to the latent heat during the condensation of metal vapor [108]. This also forms a side contact but with strong bonds (atomic bonds) between compound contact and semiconductor.

In the planar-geometry contact [109], the simplest model suggests that the electron SBH is given by:

$$\phi_b = \Phi - \chi \tag{5.14}$$

where Φ is the work function of metal-compound contact and χ is the semiconductor electron affinity as illustrated in Fig. 5.18d. The electrical charge flow across the contact-semiconductor interface equals the contact work function with

semiconductor Fermi-level and causes the conduction and valence band-edge bending near the interface. This band-edge bending is associated with a depletion (or accumulation) region and associated with a width given by:

$$W = \sqrt{\frac{2\varepsilon\phi_b}{nq}} \tag{5.15}$$

where ε is the dielectric constant of semiconductor, *n* is the dopant density, and *q* is the electron charge. In the presence of a Schottky barrier, the transport mechanisms are thermionic emission, tunneling through the barrier, and the electron-hole recombination in the depletion region. Usually, the electron-hole recombination current is much smaller than the other two, and the thermally excited tunneling current density can be expressed as [110]:

$$J_{t} = \frac{A^{*}T}{k} \int_{0}^{\infty} \tau(E) \cdot e^{-(E+q\varphi_{s})/kT} dE \times \left[1 - e^{-qV_{f}/kT}\right]$$
(5.16)

where A^* is the Richardson constant, k is the Boltzmann constant, T is the temperature, and E is the conduction band-edge energy. $\tau(E)$ is the tunneling probability for carriers, V_f is the applied forward bias, and $q\varphi_s$ is the potential energy of the charge carriers relative to the Fermi level. And therefore the contact resistivity can be calculated as [111]:

$$\rho_c = \left(\frac{\partial J}{\partial V}\right)^{-1} \bigg|_{V=0} \tag{5.17}$$

In the end-bonded contact, the depletion width was found to be larger than that in planar contact with same doping density and SBH [112]. This is related to the size-dependent fringing field in between metal contact and semiconductor NW surface. In small NWs, the strong fringing field makes the electric field lines near the contact interface incline to the ambient around the NW, causing a week electric field inside the NW. The reduced electric field screening in the small NWs results in larger depletion width, smaller tunneling current, and consequently larger contact resistivity. Shown in Fig. 5.19 are the simulation results of band-edge diagrams and contact resistivity changes versus NW radius, comparing the end-bonded contacts in NW (NW-3D contact and NW-1D contact) to planar-geometry contact [112]. It can be found that the contact resistivity of NW-1D contact is less vulnerable to change of NW size than that of NW-3D contact, indicating the advantages of forming metal-semiconductor compounds contacts inside the NW channels. In principle, high contact doping can reduce the depletion width and bring down the contact resistivity.

In the side contact, the band realignment due to charge transfer is weak due to the limited available depletion width in the NW cross section. Theoretical studies [113] of the side contact to NW device suggested that the nanoscale dimension of the NWs



Fig. 5.19 Schematic illustrations of different contact geometries to NWs: (**a**) NW-3D metal contact, (**b**) NW-1D metal contact, and (**c**) planar contact. (**d**) Simulated energy band-edge diagrams for different contact geometries. (**e**) Contact resistivity vs NW radius for different contact geometries at temperatures equal to 91 and 300 K, respectively. (Reproduced with permission from Ref. [112]. Copyright 2008 American Institute of Physics)

prevents the energy band edge from reaching their asymptotic value and instead presents only a weak band bending. Shown in the Fig. 5.20 are the simulated results of band bending and contact resistance for a heavily doped Si NW (1×10^{19} cm⁻³) with side contact. The results indicate that the conventional strategy of heavily doping the semiconductor to obtain Ohmic contacts breaks down as the NW diameter is reduced. A dramatical increase of contact resistance is expected for small NWs, as shown in Fig. 5.20c. By modeling the density of states using 1D equation in NW structures, the authors found that the quasi-1D system (NWs) requires almost 2 orders of magnitude larger density of pinning states compared with the bulk interface for the same effect of Fermi-level pinning, meaning that NWs are generally free of contact Fermi-level pinning for very small diameters. This in principle applies for end-bonded contacts as well.

In experimental measurements, the contact resistance between the compound contact and the semiconductor is sometimes misinterpreted. This is because the conventional four-probe technique can only contact resistance between metal/compound interface, but not the important compound/semiconductor interface. Transmission line measurement (TLM) is therefore a more preferred method, by patterning multiple metal pads with various spacing on a single NW channel followed by a short thermal annealing to form compound contact. An example is shown in Fig. 5.21 for TLM results on Ge/Si core/shell NWs with patterned Ni pads [114]. The fabrication was conducted on a 50 nm thick SiN_x membrane, so that after thermal annealing, the unreacted semiconductor NW segments can be precisely measured under TEM. As shown in Fig. 5.21, the contact resistance between NiGe_xSi_y and Ge/Si NW is below 10 k Ω , which is significantly smaller than typical resistance values of a NWFET device made on the same type of NWs and operating at maximum transconductance. This suggested that the contact resistance was negligible in these Ge/Si core/shell NWFET performance analysis and mobility extraction.



Fig. 5.20 Simulated energy band-edge bending across Si NWs (doping of 1×10^{19} cm⁻³) with side contact for diameters of (**a**) 40 nm and (**b**) 10 nm. (**c**) The normalized resistance as a function of NW diameter. (Reprinted with permission from Ref. [113]. Copyright 2006 American Physical Society)

5.4.3 Ultrashort Channel Devices

Enhanced NW FET performance is enabled with ever-smaller channel lengths that can provide high on-current drives. The transistor channel length is usually defined by the metal gate width (in a gate-first self-aligned process) or the distance between its S/D electrodes, both of which requires expensive e-beam lithography tools or sophisticated photolithography techniques. The metal-semiconductor compound contact formation provides a lithography-free method to achieve ultrashort channel lengths in NW channels with controlled metal-semiconductor reactions. Figure 5.22 summarizes the prominent researches that demonstrated ultrashort NW channels with two terminal contacts. The most commonly used way was to monitor the metal-semiconductor NW reactions in situ inside a TEM or SEM chamber, and the ultrashort channels have been achieved in Si [72], Ge [76], and Ge/Si core/shell [17] NWs.

Joule heating-assisted nickel silicide reaction is shown in Fig. 5.22d–e, with the channel length monitored by the current measurements across the NW [115]. During



Fig. 5.21 NW resistance as a function of non-reacted semiconductor channel lengths. The contact resistance in Ge/Si core/shell NWs is extracted to be below 10 k Ω , which is much smaller than the typical resistance of the NW FET operating at maximum transconductance (histogram peaks at 100–150 k Ω). (Reprinted with permission from Ref. [114]. Copyright 2014 American Chemical Society)

this process, voltage V_1 and V_2 were applied on the metal strip at one side of the NW, and the joule heat peaked at the strip center and induced the Ni diffusion into the Si NW. The voltage drop across the NW, equaling to $(V_1 + V_2)/2$, introduced a current flow that was recorded to monitor the silicide reaction process. Silicide could also form at the other end of the Si NW by applying V_1 and V_2 on the opposite metal strip. Due to the Schottky barrier between silicide and Si, the recorded current through Si NW was low (dominated by thermionic emission) in long channels and increased slowly as channel length decreased. When the channel length was below 50 nm, the device showed a dramatic current increase due to the carriers effectively tunneling through Schottky barrier. With carefully monitored channel current, an ultrashort channel length of 8 nm was achieved.

It has also been found that the compound contact formation in NW channels can introduce tremendous strain in the semiconductor channel [38, 67]. In the study of Ni₂In_{0.53}Ga_{0.47}As contact formation in In_{0.53}Ga_{0.47}As NW, we observed a quasi-hydrostatic compressive stress exerted on the non-reacted In_{0.53}Ga_{0.47}As channel, as shown in Fig. 5.23a. Inside the interfacial plane, formed Ni₂In_{0.53}Ga_{0.47}As has a smaller lattice contact than that of In_{0.53}Ga_{0.47}As, while in the direction perpendicular to the interface, volume expansion in Ni₂In_{0.53}Ga_{0.47}As phase introduced another compressive stress to the channel. The strain gradually vanished far from the interface (>100 nm) but caused a large energy bandgap change of In_{0.53}Ga_{0.47}As at the contact interface (shown in Fig. 5.23b). In ultrashort NW channels, the strain could build up even higher (shown in Fig. 5.22f).²⁵

To characterize the performance of the ultrashort channel device, we firstly monitored the NiSi NW reactions in TEM chamber through in situ heating, until



Fig. 5.22 (a) PtSi/Si/PtSi NW with Si length of 8 nm. Reprinted with permission from Ref [72]. Copyright 2008 American Chemical Society. (b) Ultrashort channel formed in Ge/Si core/ shell NW. Reprinted with permission from Ref. [17]. Copyright 2014 IOP Publishing. (c) $Cu_3Ge/Ge/Cu_3Ge$ NW with Ge length of 15 nm. Reprinted with permission from Ref [76]. Copyright 2009



Fig. 5.23 (a) Out-of-plane and in-plane strains of $In_{0.53}Ga_{0.47}As$ as a function of distance from the interface with nickelide contact in $In_{0.53}Ga_{0.47}As$ NW channel. (b) The calculated band-edge energies as a function of distance along x-axis based on elastic theory that incorporates deformation potentials obtained from local density functional theory [116]. The estimated bandgap of $In_{0.53}Ga_{0.47}As$ near the InGaAs/nickelide interface is ~1.26 eV in this case. (Reproduced with permission from Ref. [67]. Copyright 2015 American Chemical Society)

reaching a channel length of 17 nm. Then, 10 nm HfO₂ was deposited on top as a gate dielectric, followed by the Ti gate deposition. The ultrashort channel device shows higher on-currents than those with longer channel lengths but with higher off-state current too because of the much larger NW diameter compared with the channel length (Fig. 5.24b), which enforced stronger short channel effects. The dependence of maximum transconductance, g_m , versus the channel length, L_G , is shown in Fig. 5.24c, and the performance gain with down-scaled transistor channels starts to saturate below 100 nm. This is because the Ni-silicide/Si SB contact resistance starts to dominate the on-state conduction at short channel lengths. Figure 5.24c inset shows an energy band-edge diagram of a Si NW SB FET in the on-state with a large potential drop across the contact SB and comparatively much smaller effective carrier-driving potential drop along the channel. This suggests that the SB contact engineering is vital to best fulfill the advantages of short channel SB-FETs.

Fig. 5.22 (continued) American Chemical Society. (**d** and **e**) Joule heating-assisted nickel silicide formation in Si NW with ultrashort channel length of 8 nm. Reproduced with permission from Ref [115]. Copyright 2011 American Chemical Society. (**f**) NiSi/Si/Si NW formed by anneal point-contacted Ni to Si NW. The channel strain was measured in those ultrashort channels. (Reproduced with permission from Ref. [38]. Copyright 2007 American Chemical Society)



Fig. 5.24 (a) TEM image of a Si NW FET device with 17 nm channel length. Scale bar is 1 μ m. (b) $I_d - V_g$ characteristics of Si NW FETs with different channel lengths at $V_d = -0.1$ V at linear (left y-axis) and log (right y-axis) scales. Inset is a schematic of the ultrashort channel Si NW FET device. (c) Channel length-dependent device performance. Inset is the energy band-edge diagram of Si NW SBFET in on-state. (Reproduced with permission from Ref. [26]. Copyright 2012 American Chemical Society)

5.5 Conclusions

In this chapter, we discussed compound contacts to NW transistors that are formed by solid-state reactions between metal and semiconductor NWs. We introduced the observed phases of compound contacts formed in Si, Ge, and III–V NWs and discussed in detail about the multiphase coexistence in Si NW system and the quaternary compound phase analysis in III–V NW system. Then, we discussed the kinetic process during this solid-state reaction and proposed a model to distinguish the rate-limiting steps and to extrapolate the kinetic parameters. We then reviewed the dynamic process of the atomic-scale ledge nucleation and movements, together with the special case when defects were present. These discussions paved the way for the introduction of electrical properties of NW transistors with these compound contacts. Different applications of these compound contacts were summarized, including tunable SBH electrical contact, spin-polarized carrier injection, infrared light detection, etc. Different contact geometries in NWs were discussed together with their band alignment and charge injection properties. Several reports on ultrashort channel devices were summarized where the channel lengths were controlled by the compound contact reaction. These comprehensive studies demonstrate the promise of compound contacts in nanoscale electronics.

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