

Precursors for chemical vapor deposition of NiSi

Masato ISHIKAWA, Takeshi KADA, Hideaki MACHIDA, Yoshio OHSHITA¹, and Atsushi OGURA²

Tri Chemical Laboratories Inc.

8154-217 Uenohara, Uenohara-machi, Kitatsuru-gun, Yamanashi 409-0112, Japan

Phone: +81-554-63-6600, Fax: +81-554-63-6161, e-mail: masato.ishikawa@trichemical.com

¹Toyota Technological Institute

2-12-1 Hisakata, Tenpaku-ku, Nagoya 468-8511, Japan

Phone: +81-52-809-1876, Fax: +81-52-809-1879, e-mail: ohshita@toyota-ti.ac.jp

²Silicon Systems Res. Labs, NEC Corp.

1120 Shimokuzawa, Sagamihara-shi, Kanagawa 229-1198, Japan

Phone: +81-42-771-2394, Fax: +81-42-771-2481, e-mail: a-ogura@cd.jp.nec.com

1. Introduction

In the development of metal oxide semiconductor field effect transistors (MOSFETs), the contact resistance of the source and drain (S/D) affects significantly on their properties. Titanium disilicide (TiSi₂), or cobalt disilicide (CoSi₂) have been widely used to reduce the resistance. However, even lower resistivity and process temperature are required for future CMOS devices. Therefore, much research has been focused on nickel monosilicide (NiSi), which has advantages in low resistance (~14 μΩ cm), stability upto 700 °C, and lower silicon consumption than other silicides.[1,2] In addition, NiSi is a candidate as a material for metal-gate electrode.[3]

In the conventional ULSI process, so-called salicide (self-aligned silicide) process has been used to obtain the contacts at S/D and gate electrode, simultaneously. In the process, metal film is deposited by sputtering method and then annealed to form silicide. However, the conformal formation of the silicide on the 3-D structure may be desired in the future finite devices. Moreover, selective deposition may provide further advantages for the contact on ultra-shallow junctions. The requirements of the conformality and selectivity can be satisfied very often by chemical vapor deposition (CVD) technique. The performance of CVD and the properties of deposited film are usually affected strongly by the precursors used in the

system. Therefore, the choice of metal precursors is very important. The precursor should have transportability for stable supply, and moderate reactivity to maintain good step coverage, and so on. Although various nickel precursors are proposed, most of them are solid at 100 °C, and have low vapor pressure. Therefore, to find superior nickel precursors for NiSi CVD, we synthesized some and clarified them through deposition experiment. In this study, we mainly studied on the synthesis of bis-methylcyclopentadienyl-nickel (MeCp₂Ni), which had high vapor pressure, and the deposition of NiSi using it.

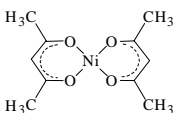
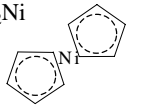
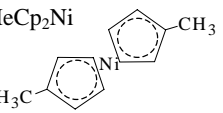
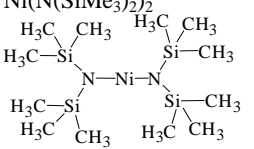
2. Synthesis

Popular nickel precursors including β-diketonate and cyclopentadienyl types are outlined in Table I. Films containing nickel could be deposited using them, but it should not be easy since the melting points of acac₂Ni and Cp₂Ni are above 150 °C. [4-6] In the case of organometallic compounds with ionic bonds like an organo-nickel, the characteristics such as small molecules, the organic ligands covering on the cationic Ni(II) atom, and low packagability of crystal may be required to obtain high vapor pressure. Precursors with β-diketone has strong intermolecular interaction. Therefore Cp type precursors may be more suitable for NiSi. Therefore, we focused on methylcyclopentadiene (MeCp) consisting of hydrocarbons. However, since nickel atom is well veiled by MeCp, MeCp₂Ni may have lower reactivity with other molecules and substrate surface than that for Cp₂Ni. It can also be pointed out that the MeCp₂Ni may show self thermal decomposition at lower temperature than that of Cp₂Ni, since methyl group on MeCp₂Ni causes steric hindrance. We therefore synthesized and characterized MeCp₂Ni first, using traditional method.

The precursor and its purity were identified by gas chromatography mass spectra (GCMS), and the physical volatility was measured with thermo gravimetry differential thermal analysis (TGDTA). The vapor pressure of the nickel precursor was determined with the saturated gas technique, where the setup was similar to the CVD bubbling system. MeCp₂Ni was transported with carrier gas at constant pressure and temperature. The vapor pressure curve was determined by the weight decreasing at each bubbling condition. MeCp₂Ni had low viscosity and high vapor pressure of 1 Torr at 73 °C. The following expression was estimated through Clausius-Clapeyron plots,

$$\log p = 9.17 - 3,311/T$$

Table I CVD precursors for nickel

(1) acac ₂ Ni		Bluegreen solid m.p. 238 (decomp.)
(2) Cp ₂ Ni		Green solid m.p. 173-174
(3) MeCp ₂ Ni		Green solid m.p. 34-35
(4) Ni(N(SiMe ₃) ₂) ₂		Deepred liquid (Easily decompose at r.t.)

where p and T are the vapor pressure (Torr) and absolute temperature (K). (Fig.1). As expected, MeCp_2Ni had high vapor pressure. This seemed to be promising, however to verify this, we tried to move CVD deposition using this precursor.

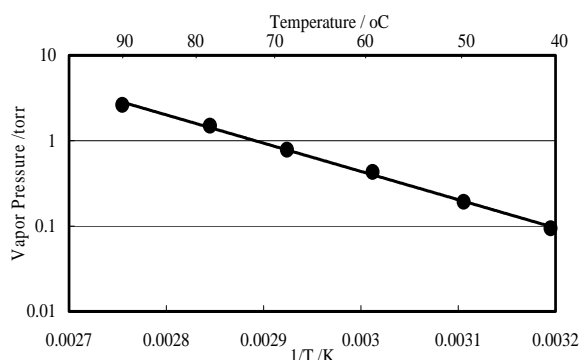


Fig. 1 Vapor pressure of MeCp_2Ni

3. Chemical vapor deposition

A cold wall type low pressure CVD (LPCVD) system was used for the NiSi deposition. Substrates were p-type Si (100), or $\text{SiO}_2/\text{Si}(100)$. The deposition conditions were as shown in Table II.

Table II Deposition conditions for LPCVD

Substrate	p-Si(100)	
Pressure /Pa	Chamber	100
Depo. time /min		0.1--180
Temperature /	Substrate	200--600
	Precursor's bottle	50--70
	Path	70--100
Flow rate/sccm	$(\text{MeCp})_2\text{Ni}$	10 -- 20
	1% $\text{Si}_3\text{H}_8/\text{H}_2$	0 --40

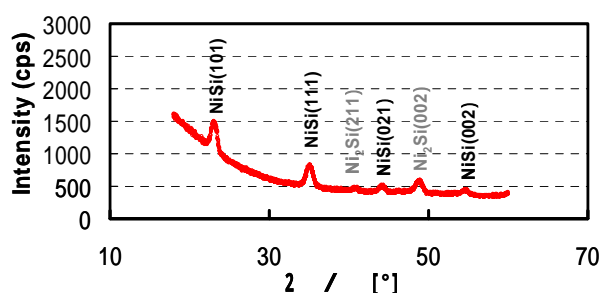


Fig. 2 XRD spectrum of deposited film at 300 °C

First, the film was deposited on the Si substrate at 300 °C by using the $\text{MeCp}_2\text{Ni}/\text{H}_2$ gas system. XRD spectrum obtained from the deposited film indicated that the main phase was NiSi (Fig. 2). The present precursor was easily decomposed even at low temperature of 300 °C and the deposited Ni reacted with the substrate Si, resulting in the NiSi formation.

To prevent the Si consumption, the silicon source was also injected during the deposition. Here, Si_3H_8 was used as a Si precursor. Si_3H_8 can be expected to decompose at low temperature, compared with other silanes. Therefore, it may be suitable for NiSi deposition, in which lower process

temperature than those for other metal silicides is required. By supplying MeCp_2Ni only, the deposited nickel reacted with Si substrate (Fig.3a). On the other hand, by supplying both MeCp_2Ni and Si_3H_8 simultaneously, deposited NiSi film had flat interface without reaction (Fig.3b). Therefore, it can be concluded that the Si_3H_8 successfully prevented the Si substrate consumption through silicide reaction.

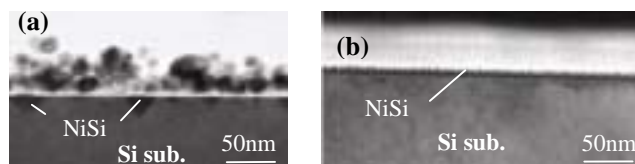


Fig.3 Cross-sectional TEM image of deposited films; Deposition (a) without Si_3H_8 , and (b) with Si_3H_8 .

Fig. 4 is a cross-sectional TEM image of NiSi film deposited on SiO_2/Si patterned substrate. The substrate was covered with conformal NiSi. The NiSi film was deposited on both surfaces of Si and SiO_2 in the present experiment.

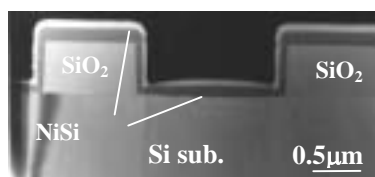


Fig. 4 Cross-sectional TEM image of deposited film; Both MeCp_2Ni and Si_3H_8 were supplied at 400 °C for 30min.

5. Conclusions

We synthesized several nickel precursors for NiSi CVD. Bis-methyl-cyclopentadienyl-nickel (MeCp_2Ni) was suitable for CVD precursor, since it was stable, and had low viscosity and high vapor pressure (1torr at 73 °C).

Resulting from XRD and cross-sectional TEM observation of the deposited film, it was confirmed that the NiSi films were successfully formed at 300 °C. Ni reacted with Si substrate, and silicides were penetrate into the Si substrate without supply of Si precursors. To prevent the Si consumption, Si_3H_8 was injected during the deposition. The deposition of NiSi film with flat interface on Si substrate was achieved. It was also confirmed that the patterned substrate was covered conformally with NiSi film showing good step coverages. Although the NiSi films were deposited on both Si and SiO_2 surfaces in the present experiment, the selective deposition only on Si should provide great advantages for ULSI application. To achieve selective deposition, higher reactivity with silicon substrate than MeCp_2Ni would be required. The smaller ligands than that of MeCp_2Ni may be effective. The precursor with smaller ligands may expose nickel atom easier, therefore nickel may easily adsorbed only at the Si surface.

References

- [1] Y.Tsuchiya, *et al.*, *Advanced Metallization Conference 2001 Proc.* (2001) p679.
- [2] P.S.Lee, *et al.*, *Microelectronic Eng.* **60** (2002) p171.
- [3] J. Kedzinski, *et al.*, *IEDM proceedings* (2002).
- [4] E.Fujii, *et al.*, *Jpn. J. Appl. Phys.*, **35** (1996) L328.
- [5] J-K.Kang, and S-W.Rhee, *J. Mater. Res.*, **15** (2000) p1828.
- [6] L.Brissonneau, *et al.*, *Chem.Vap. Deposition*, **5** (1999) p143.