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Composition control of Ni-silicide by CVD using $Ni(PF_3)_4$ and Si_3H_8

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1 Abstract

The composition of Ni-silicide is controlled by the new CVD using the $Ni(PF_3)_4/Si_3H_8$ gas system. $Ni(PF_3)_4$ is liquid at a room temperature and has high vapor pressure enough for using mass flow controller. By using Si_3H_8 as a silicon source, the Ni-silicide film is deposited at low temperatures (200ºC) and its composition is changed by varying the Si_3H_8 flow rate. V_{fb} for the Ni-silicide electrode shifts as compared with that for the pure Ni electrode and the V_{fb} shift increases as the Si composition in the film increases. We believe that this Ni-silicide CVD can be applied to metal gate fabrication in future MOSFETs.

2 Introduction

Ni-silicide is considered to be a promising candidate for gate electrode material in MOSFET. Replacing traditional poly-Si by metal such as Ni-silicide eliminates gate depletion, therefore accelerate device speed. Especially, combination using metal gate with high-k gate insulator (f.e. $Hf_xSi_{1-x}O_2$), provide superior characteristics with low leakage and high operation current. Moreover, threshold voltage (V_{th}) can be adopted by controlling composition of Ni-silicide [1]. Therefore, Ni-silicide can be used in both n- and p-type MOSFET for low-power and high-speed applications. Ni-silicide gate has been formed by so-call FUSI (fully-silicided) process, in which Ni is deposited on poly-Si film and annealed at 400 to 700ºC [1-3]. However, it may be too complicated to control the Ni-silicide composition with FUSI technique. CVD is very attractive technique for metal gate formation, because it is simple and easy to control both composition and doping. However, traditional CVD precursors for Ni include Carbon in a molecule; therefore the deposited film usually has a high resistance. This is not appropriate for gate electrode application. Recently, we proposed a new Ni precursor for LSI metallization, tetrakis (trifluorophosphine)nickel(0); $Ni(PF_3)_4$ [4]. In this study, we propose Ni-silicide composition control method; CVD using $Ni(PF_3)_4$ and Si_3H_8.

Ni-silicide precursor

Ni precursor

$Ni(PF_3)_4$ was used as a Ni source. It is transparent liquid and has high vapor pressure (215Torr at 30ºC; Fig. 1), which make it possible to use mass flow controller (MFC) for the source supply. The $Ni(PF_3)_4$ does not have carbon atoms in its molecule structure; and pure Ni thin film can be deposited by CVD [4]. we developed a new method to synthesized $Ni(PF_3)_4$ from Cp_2Ni and PF_3 with high yield over 80%. The metal purity was less than 10 ppm, which was determined by inductively coupled plasma mass spectrometry (ICP-MS).

Silicon precurosr

Si_3H_8 was used as a silicon precursor. Lower temperatures are required for Ni-silicide formation than those for other metal silicide, and then Si precursor should decompose at low temperature. Si was incorporated by CVD using the $(MeCp)_2Ni/Si_3H_8$ gas system[5]. Therefore, it may be suitable for the present Ni-silicide CVD.

Ni-silicide deposition

Schematically illustration of the CVD apparatus used in this study is shown in Fig. 2. A cold-wall low pressure CVD (LPCVD) reactor was used for the present study. The steel deposition chamber was evacuated with turbo molecular and rotary pumps. The deposition pressure was controlled using the orifice. The substrate was heated by a heating element mounted below it. $Ni(PF_3)_4$ and Si_3H_8 (1% diluted by 99% H_2) were introduced into the deposition chamber by using MFCs. The $Ni(PF_3)_4$ container temperature was kept at 50ºC. The typical deposition temperature, pressure, were, 200ºC, 30Pa, respectively. The $Ni(PF_3)_4$ flow rate was 4 sccm. Si_3H_8 flow rate was changed 0 to 60 sccm for varing Ni-silicide composition. The Ni-Si composition was measured by Rutherford Backscattering Spectrometry (RBS), X-ray photospectroscopy (XPS). Surface morphology and deposition rate of deposited films were observed by scanning electron microscopy (SEM). C-V measurement was carried out for evaluating flat-band voltage (V_{fb}) shift.

Results and Discussion

Composition of Ni-silicide film deposited at 200ºC shown in Fig. 3, which was obtained by RBS. Large amount of Si was incorporated in the grown film. The composition of Ni-silicide was changed as controlling the Si_3H_8 flow rate (Fig. 4). Here, the composition was estimated form peak area ratio of Ni(2p) and Si(2p) signals obtained by XPS.

When the Ni film was deposited without Si_3H_8 injection, the surface morphology was rough. By supplying Si_3H_8, the surface becomes smooth (Fig. 5). Here the Ni-silicide film was deposited at 200ºC with 10 sccm Si_3H_8.

The C-V curves for 100nm SiO_2 p-MOS are show in Fig. 6. V_{fb} for the Ni-silicide electrode shifts as compared with that for the pure Ni electrode and the V_{fb} shift increases as the Si composition in the film increases.

We conclude that the V_{th} of MOS can be controlled by changing the composition of Ni-silicide by CVD using the $Ni(PF_3)_4$ and Si_3H_8 gas system.

References

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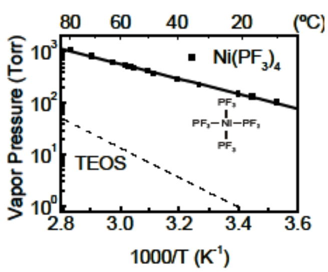

Fig. 1 Vapor pressure of $Ni(PF_3)_4$. It is liquid at room temperature and has high vapor pressure enough for MFC use.

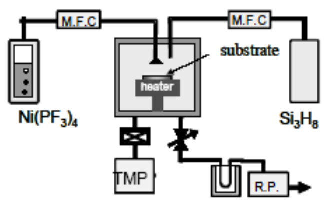

Fig. 2 CVD set-up for Ni-silicide formation.

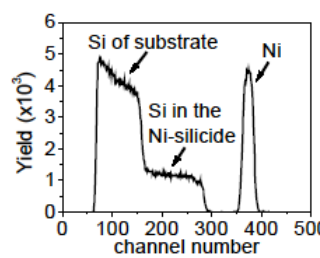

Fig. 3 Ni/Si composition measured by RBS. Ni-silicide was deposited at low temperature (200ºC)

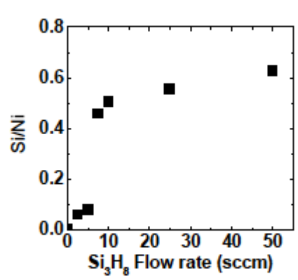

Fig. 4 Ni/Si composition. The amount of Si in films increased as Si_3H_8 flow rate increased.

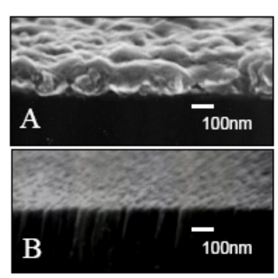

Fig. 5 A) Ni film, B) Ni/Si film. Surface morphology became smooth by injection of Si_3H_8.

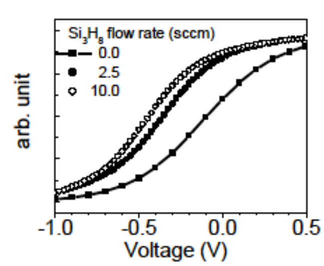

Fig. 6 C-V charactaristics of Ni-silicide/SiO_2 and Ni/SiO_2. The amount of V_{fb} shift increased as the Si composition in the Ni-silicide increase.