NiAl as a Potential Material for Liner- and Barrier-Free Interconnect in Ultrasmall Technology Node

Linghan Chen a), Daisuke Ando a), Yuji Sutou a), Daniel Gall b), and Junichi Koike a)*

a) Department of Materials Science, Tohoku University, Sendai 980-8579, Japan
b) Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

Because of aggressive down scaling of the dimensions of future semiconductor devices, they will suffer from increased line resistivity and resistance-capacitance delay. In this work, NiAl thin films are investigated as a potential liner- and barrier-free interconnect material. The results show that NiAl has strong adhesion, does not undergo interdiffusion with SiO₂, and has a favorable resistivity size effect. These features suggest that NiAl is a good candidate to replace Cu as a liner- and barrier-free interconnect for linewidths below 7 nm.

*Author to whom correspondence should be addressed: koikej@material.tohoku.ac.jp
Conventional Cu interconnects for large-scale-integrated devices face a serious challenge because the aggressive down scaling of such devices significantly increases the interconnect resistivity. The resistivity rise is due, first, to the interconnect linewidth becoming shorter than the electron mean free path (EMFP) of Cu and, second, to the presence of liner and barrier layers occupying the line volume. A liner layer of Co, Ru, Ti, or Ta is necessary to promote good wettability so that Cu fills the gaps in pre-formed trenches and vias in the dielectric [1, 2]. A barrier layer of TiN or TaN is necessary to prevent interdiffusion with the dielectric [3–5]. Various works have focused on mitigating the problem of resistivity increasing with narrowing linewidth, including barrier-thickness reduction to 1.2 nm and embedded-barrier formation within the dielectric by the use of Mn silicate [6–8]. More recently, the use of graphene or h-boron-nitride has been reported to act as an efficient barrier layer with less than 2 nm thickness [9–12]. Alternatively, extensive works have searched for new interconnect metals that require no liner or barrier layers and have a small EMFP–bulk-resistivity product ($\lambda \times \rho_o$). Based on the calculated $\lambda \times \rho_o$ values, Gall proposed W ($\lambda \times \rho_o = 8.20 \times 10^{-16} \Omega \text{m}^2$), Mo ($5.99 \times 10^{-16} \Omega \text{m}^2$), Co ($7.31/4.82 \times 10^{-16} \Omega \text{m}^2$), and Ru ($5.41/3.81 \times 10^{-16} \Omega \text{m}^2$) [13]. In fact, Co and Ru have been a subject of intense research. For films less than 7 nm thick, the resistivities of Co and Ru are similar in magnitude to that of Cu [14, 15]. Tests of time-dependent dielectric breakdown showed that Ru does not drift but Co does. Electromigration tests showed that Ru is much more reliable than Cu and that Co is slightly more reliable than Cu. Although Ru seems to be a promising candidate to replace Cu, it requires a 0.3-nm-thick TiN layer to ensure adhesion and to prevent delamination during chemical mechanical polishing [16]. Therefore, liner- and barrier-free metallization has yet to be achieved.

In this work, we focus on a NiAl intermetallic compound with an ordered body-centered cubic (bcc) structure. NiAl has a bulk resistivity of 9 $\mu\Omega \text{cm}$ [17, 18] and is a well-known heat-resistant material with a high melting point of 1638 °C [19], which means that reliable electromigration can be expected. Meanwhile, NiAl has a large cohesive energy of $−679 \text{kJ/mol}$ [20], so the interdiffusion and detrimental
reaction with Si and SiO2 may be suppressed. Furthermore, Al oxide has a heat of formation of $-1678$ kJ/mol, which is much greater than that of SiO2 ($-911$ kJ/mol) [21], so there is a tendency for Al atoms to bond with O atoms at the NiAl/SiO2 interface, possibly leading to good adhesion. More importantly, Tabatabaie et al. [22] measured the electrical resistivity of thin NiAl films sandwiched between AlAs/GaAs layers and found a remarkable scalability of resistivity (314 $\mu$Ω cm for a thickness of 1.5 nm). Therefore, NiAl is a potential candidate for liner- and barrier-free interconnect material. In this work, we investigate adhesion strength, electrical resistivity, and interdiffusion of blanket NiAl films, without liner or barrier layers, on SiO2/Si substrates. The resistivity as a function of linewidth is also calculated and compared with that of Cu with liner-barrier layers.

The substrates consisted p-type Si wafers coated with 20- or 100-nm-thick thermally grown SiO2. Films of NiAl (with 48 to 53 at.% Ni) were deposited directly onto the SiO2 substrates by co-sputtering of pure Ni and Al targets with an Ar gas flow of 15 sccm, maintaining a working pressure of $6 \times 10^{-1}$ Pa. Annealing was done at various temperatures by using a tube furnace in a mixed-gas atmosphere of Ar + 5% H2. The film thickness was measured by using an atomic force microscope. The crystal structure was examined by using $\theta$-2$\theta$ x-ray diffraction (XRD) with Cu $K\alpha$ radiation. To evaluate the adhesion strength of NiAl films on SiO2 substrates, tape tests were done in accordance with ASTM D 3359-79 [23]. The film resistivity was measured by using the van der Pauw method. The microstructure and composition profile were investigated by cross-sectional transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS). The cross-sectional TEM samples were prepared by bonding two samples face to face with epoxy, followed by mechanical thinning and ion-beam thinning. The possibility of interdiffusion was examined by measuring the shift of the flatband voltage $V_{fb}$ in the capacitance-voltage (CV) curves of NiAl/SiO2/p-Si metal-oxide-semiconductor (MOS) capacitors before and after thermal stress (TS) or bias thermal stress (BTS). To form Ohmic contacts, a 500-nm-thick Al layer was deposited by sputtering on the backside of Si after removing the oxide with diluted HF. The top-gate
An electrode of 150-nm-thick NiAl was formed by using a lift-off photolithography process [24]. Pre-annealing was done at 300 °C for 30 min to eliminate oxide charges. TS tests were done in a tube furnace in the Ar + 5% H2 gas atmosphere at temperatures of 400 to 600 °C for 10 min. BTS tests were done at a bias field of 3 MV/cm at 250 °C for various times in the Ar + 5% H2 gas environment. Both TS and BTS were imposed cumulatively on the samples. The line resistivities of NiAl and Cu were calculated as a function of linewidth. A square shape was assumed for the line cross section, and the grain size was set equal to the linewidth. The Fuchs–Sondheimer [25] and Mayadas–Shatzkes [26] models were used to account for surface scattering and grain-boundary scattering, respectively, with a surface specular factor $p = 0$ and a grain-boundary reflection factor $R = 0.4$ for both NiAl and Cu [27]. The EMFP $\lambda$ of NiAl was determined from first principles, following the procedure described in Ref. [13]. For this purpose, the Fermi surface and the wave-vector-dependent Fermi velocity were obtained from density functional theory by using a cubic two-atom NiAl unit cell with a 0.2884 nm lattice constant, which was determined from volume relaxation.

Figure 1 shows XRD results for a NiAl (50 at.% Ni) blanket film before and after cumulative annealing at 250, 400, and 500 °C for 30 min. In this paper, unless otherwise specified, NiAl corresponds to NiAl with 50 at.% Ni. The formation of a B2-type (an ordered bcc) NiAl intermetallic compound is indicated by the appearance of a 100 superlattice peak and a 110 fundamental peak. After annealing at temperatures up to 500 °C, the full width at half maximum (FWHM) of the 110 fundamental peak decreases by 0.06°, 0.08°, and 0.12°, respectively, compared with the FWHM of the as-deposited sample, which suggests grain growth. Although not shown here, the cross-sectional TEM images before and after annealing at 500 °C confirm the growth of columnar grains from 8 to 16 nm in average width, and from 40 to 150 nm in average length.

Tape tests show no delamination for all NiAl samples before and after annealing at different temperatures for 30 min, indicating that NiAl adheres well to SiO2 without requiring a liner layer. Figures
2(a) and 2(b) show the cross-sectional TEM images of the NiAl/SiO$_2$ interface region before and after annealing at 500 °C, respectively, and the corresponding EDS results are shown in Figs. 2(c) and 2(d). The relatively broad transition region in the EDS profile is due to the convolution and dispersion of a probing electron beam with a few nm in diameter. One also notices small signals from Si and O in the NiAl layer. This is most likely due to Si redeposition during TEM sample preparation by ion milling and to the partial oxidation of the TEM sample, respectively. Both the TEM images and EDS results show no notable difference before and after annealing, suggesting that the good adhesion between NiAl and SiO$_2$ is due to strong chemical bonding on an atomic scale rather than the formation of a reaction layer by diffusion.

Figures 3(a) and 3(b) show CV curves after cumulative TS and cumulative BTS, where the measured capacitance $C_{MOS}$ is normalized by the oxide-accumulation capacitance $C_{OX}$ at a gate voltage of $-10$ V. Figures 3(c) and 3(d) show the corresponding flatband voltage obtained by plotting $1/(C_{MOS}/C_{OX})^2$ versus gate voltage. After TS and BTS, no negative shift of $V_{fb}$ appears, indicating no diffusion of Ni and Al ions into SiO$_2$. A very small positive shift appears with increasing TS temperature and BTS time, which may be related to Si-O-Al bond formation at the NiAl/SiO$_2$ interface [28]. Combining with the TEM and EDS results, we conclude that NiAl does not require liner or diffusion-barrier layers.

Figure 4 shows the electrical resistivity of 260-nm-thick NiAl films as a function of Ni composition before and after cumulative annealing for 30 min. The minimum values of resistivity occur at the stoichiometric composition of 50 at.% Ni. The higher resistivity beyond stoichiometry is attributed to electron scattering by constitutional defects [17]. The film resistivity decreases with increasing annealing temperature, owing to grain growth and defect annihilation. The resistivity reaches 10.1 $\mu\Omega$ cm after annealing at 500 °C at the stoichiometric composition, which is very close to the reported bulk resistivity of 9 $\mu\Omega$ cm.
Figure 5 shows the calculated resistivity as a function of linewidth for NiAl without a liner or barrier, for Cu without liner or barrier, and for Cu with a 2-nm-thick liner and barrier. The calculated $\lambda \times \rho_o$ product for NiAl is $7.34 \times 10^{-16}$ $\Omega$ m$^2$, as determined by numerical integration of the Fermi surface using a constant-$\lambda$ approximation [13]. A $60 \times 60 \times 60$ $k$-point grid converges with a computational uncertainty of 0.1%. The use of the reported bulk resistivity of $\rho_o = 9$ $\mu$Ω cm [17, 18] gives a predicted EMFP of $\lambda = 8.15$ nm for NiAl. Meanwhile, $\rho_o = 1.7$ $\mu$Ω cm and $\lambda = 39$ nm are used for Cu. When the line resistivities without liner or barrier layers are compared, the resistivity of NiAl is always greater than that of Cu. However, Cu cannot be used without liner and barrier layers whereas the present work finds that NiAl needs no liner or barrier. Thus, below the linewidth of 7 nm, the resistivity of NiAl is expected to be less than that of Cu with the liner and barrier layers.

To summarize, NiAl adheres well to SiO$_2$ according to tape tests and no interdiffusion occurs in thermal-stress and bias-thermal-stress tests. These results suggest that NiAl is a promising interconnect material that would not require liner or barrier layers. The calculated product $\lambda \times \rho_o$ of NiAl is $7.34 \times 10^{-16}$ $\Omega$ m$^2$, yielding an EMFP of 8.15 nm with a bulk resistivity of 9 $\mu$Ω cm. For linewidths less than 7 nm, the small $\lambda \times \rho_o$ product and the liner- and barrier-free structure reduce the resistivity of NiAl below that of conventional Cu with liner and barrier layers.

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**References**


Figure Captions

FIG. 1. Results of XRD $\theta - 2\theta$ scan of 150-nm-thick NiAl films before and after annealing at different temperatures for 30 min.

FIG. 2. Cross-sectional TEM images of NiAl/SiO$_2$ interface together with EDS intensity profiles of (a), (c) as-deposited and (b), (d) after annealing at 500 °C for 30 min.

FIG. 3. Normalized CV curves of NiAl/SiO$_2$/p-Si MOS capacitors and flatband voltage $V_{fb}$ before and after (a), (c) thermal stress and (b), (d) bias thermal stress.

FIG. 4. Resistivity as a function of Ni concentration for 260-nm-thick NiAl film on SiO$_2$/Si substrate with cumulative annealing for 30 min, at temperatures up to 500 °C.

FIG. 5. Resistivity as a function of line width for NiAl line without liner or barrier layers and of a Cu line with and without 2-nm-thick liner-barrier layer.
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