ARTICLE IN PRESS



1

4

5

6 7

8 9 Available online at www.sciencedirect.com



Thin Solid Films xx (2004) xxx-xxx



www.elsevier.com/locate/tsf

2 Effects of silicon nitride interlayer on phase transformation and adhesion 3 of TiNi films

Yongqing Fu^{a,b,*}, Hejun Du^{a,b}, Sam Zhang^b, Soon Eng Ong^b

^aAdvanced Materials for Micro and Nano Systems Programme, Singapore-Massachusetts Institute Technology (MIT) Alliance, 4 Engineering Drive 3,

Singapore 117576, Singapore

^bSchool of Mechanical and Production Engineering, Nanyang Technological University, Singapore 639798, Singapore

Received 20 February 2004; received in revised form 23 August 2004; accepted 30 September 2004

10 Abstract

TiNi films with different Ti/Ni ratios were deposited on Si substrates with and without silicon nitride interlayer. Near-equiatomic TiNi films were found to have the lowest residual stress and the highest recovery stress regardless of the existence of silicon nitride interlayer. The addition of silicon nitride interlayer between film and Si substrate did not cause much change in phase transformation behavior as well as adhesion properties. X-ray photoelectron spectroscopy (XPS) analysis revealed that there is significant interdiffusion of elements and formation of Ti–N and Si–Si bonds at TiNi film/silicon nitride interface. Scratch test results showed that adhesion between the TiNi film and substrate was slightly improved with the increase of Ti content in TiNi films.

17 © 2004 Published by Elsevier B.V.

18 Keywords: TiNi; Adhesion; Sputtering; Shape memory; XPS; Silicon nitride

19

20 1. Introduction

21Shape memory alloys (SMAs) possess an array of 22desirable properties: high power to weight (or force to volume) ratio, thus the ability to recover large trans-2324formation stress and strain upon heating and cooling, peudoelasticity (or superelasticity), high damping capacity, 2526good chemical resistance and biocompatibility [1-4]. More recently, thin film SMA has been recognized as a 27promising and high performance material in the field of 28 29microelectromechanical system (MEMS) applications [5–9]. When the TiNi films are deposited on Si substrate, there 30 31exist interfacial diffusion and chemical interactions at the 32 interface whereby titanium and nickel silicides may form 33 during high temperature deposition or postdeposition

* Corresponding author. Department of Engineering, Cambridge University, Trumpington Street, Cambridge, CB2, 1PZ, UK. Tel.: +441233 343560; fax: +441233 343876.

E-mail address: yf229@cam.ac.uk (Y. Fu).

annealing [10,11]. These interfacial reaction products 34could be complex, heterogeneous and metastable, and a 35 relatively thin reaction layer could have significant adverse 36 effect on adhesion and shape memory properties. In 37 microelectronics and MEMS processes, there need electri-38cally and thermally insulating layer, sacrificial or diffusion 39 barrier layer. Thermally grown SiO₂ is often used for this 40purpose. However, adhesion of TiNi film on SiO₂ layer (or 41on glass and polymer substrate) is poor owing to the 42formation of a thin intermixing fragile and brittle TiO₂ 43layer [10]. In a significant deformation or during a 44complex interaction involving scratch, this layer is easily 45broken, thus causing large-area peeling off. Adhesion of 46TiNi films on other interlayers (such as silicon nitride, 47polysilicon, etc.) is important for their successful MEMS 48applications, but few studies have been performed so far. 49In this study, TiNi thin films with three different Ti 50contents were sputtered onto Si wafer with and without 51silicon nitride (Si₃N₄) layer. Phase transformation charac-52teristics, stress evolution and interfacial adhesion were 53studied in details. 54

^{0040-6090/\$ -} see front matter $\ensuremath{\mathbb{C}}$ 2004 Published by Elsevier B.V. doi:10.1016/j.tsf.2004.09.058

2

t1.1

Table 1

ARTICLE IN PRESS

Y. Fu et al. / Thin Solid Films xx (2004) xxx-xxx

55 2. Experimental details

56Single crystalline silicon wafers (100-type with thickness of 0.45 mm) were used as substrates. A layer of silicon 5758nitride (0.2 µm thick) were deposited using low-pressure 59chemical vapor deposition with SiH₄ and NH₃ as precursors at a high temperature of 1073 K. TiNi films with three 60 different compositions were prepared by cosputtering an 6162 equiatomic TiNi target and a pure Ti target. The base pressure of the main chamber was 1.33×10^{-5} Pa. The 63 target-to-substrate distance was 100 mm, and Ar gas 64pressure was 0.133 Pa with a flow rate of 20 sccm. Plasma 65power of the Ti target was varied in order to adjust the film 66 67 composition (see Table 1), and the substrate holder was rotated to enhance film uniformity. 68

69 Chemical compositions of the films were investigated by energy dispersive X-ray spectrometry. Measurements 7071were done on five different regions on each of the sample, and the average values are listed in Table 1. Curvature 7273changes of the film-deposited Si wafers were measured as a 74function of temperature using a Tencor FLX-2908 laser 75system with a heating and cooling rate of 1 K/min, from 76 which the stress changes were derived [12,13]. Crystalline structures of the TiNi films were characterized using 77 78 Philips PW3719 X-ray diffraction (XRD, Cu-Kα, 40 kV/ 7930 mA). Interfacial adhesion of the TiNi film on substrate 80 was assessed using a SHIMADZU SST-101 scanning scratch tester. A stylus of 15-um tip radius was used at a 81 82 load increased stepwise to a full load of 500 mN. During 83 the scratch operation, the forward speed was set at $1 \,\mu m/s$, 84 scratch speed 10 µm/s and amplitude of scanning 50 µm. A 85 sudden increase in frequency output indicated adhesion failure, and the normal load at which the damage incurs 86 87 was used as a measure of the adhesion strength. X-ray photoelectron spectroscopy (XPS) analysis was performed 88 89 on TiNi/Si and TiNi/Si₃N₄ interfaces using a Kratos AXIS spectrometer with monochromatic Al Ka (1486.71 eV) X-90 91rav radiation. TiNi film was peeled off from both Si and 92Si₃N₄/Si substrates, and the peeled-off interfaces were 93 immediately analyzed using XPS for interfacial chemistry. Wide-scan spectra were recorded in 1 eV step for all 9495samples. Detailed core level spectra of different elements 96 were recorded in 0.1 eV step. Curve fitting was performed after a Shirley background subtraction by a non-linear least 97 98square fit. The spectra were calibrated using the C 1s 99 (284.6 eV) peak as a reference. For elemental depth 100 profiling of the interfacial structure, an ion gun (Kratos



Fig. 1. XRD results of TiNi films with different Ti contents deposited on Si and Si_3N_4 interlayer: (a) on Si substrate (b) on Si_3N_4 interlayer.

MacroBeam) of 4 keV energy was used with high purity 101 Ar gas. 102

3. Results and discussions 103

Fig. 1(a) shows XRD results of the TiNi films deposited 104on Si with three different Ti contents. The dominant phase 105for the near-equiatomic film (Ti50.2Ni) is mainly martensite 106with some untransformed R-phase/austenite. For the Ti-rich 107(Ti52.5Ni) and Ni-rich films (Ti48.4Ni), the phases are a 108mixture of austenite and martensite with more contents of 109austenite. Fig. 1(b) shows XRD results of the TiNi films 110 deposited on the Si₃N₄ interlayer. There is not much 111 difference for the XRD results for TiNi films on Si substrate 112or Si₃N₄ interlayers except the relative intensities of 113

t1.2 Sputtering conditions, film thickness and composition of TiNi films [radio frequency (RF), direct current (DC)]

3	Power (W)		Deposition	Duration	Ar pressure	Film thickness (µm)	Composition (at.%)	
1	TiNi (RF)	Ti (DC)	temperature (K)	(h)	(Pa)		Ti	Ni
5	400	60	723	4	0.133	3.5	48.4	51.6
3	400	70	723	4	0.133	3.5	50.2	49.8
7	400	80	723	4	0.133	3.5	52.5	47.5

123 austenite and martensite, which is due to the differences in 124 phase transformation temperatures. All the films regardless 125 of interlayer or Ti content show martensite dominant after 126 blowing with liquid nitrogen vapor, indicating that the 127 austenite transformation start temperatures for all the films 128 are above room temperature of 293 K.

129The stress-temperature results for the TiNi films with different Ti/Ni ratios on both Si substrate and Si₃N₄ 130 interlayer are shown in Fig. 2a and b. All the stress vs. 131132temperature plots show a closed hysteresis loop. During heating, the stress increases significantly due to the phase 133transformation from martensite to austenite until the 134temperature reaches to austenite transformation finish 135temperature (A_f) . With the further increase of temperature, 136the transformation completes and generation of thermal 137stress occurs with the stress values decreasing linearly. 138During cooling, tensile thermal stress develops in TiNi 139films. When the temperature is just above martensite 140 transition start temperature (M_s) , the residual stress reaches 141its maximum. Cooling below M_s , the martensitic trans-142formation occurs and the tensile stress drops significantly 143144due to the formation and alignment of twinned martensite [5,12,13]. The curves of stress increase rate (i.e., the 145differentiated stress vs. temperature) for all the films can 146be obtained from Fig. 2, and the results are shown in Fig. 3a 147148 and b. A negative sign was applied to all the data during cooling, just to make different with those during heating 149



Fig. 2. Stress-temperature evolution curves for the TiNi films with different Ti/Ni ratios on both Si substrate and Si_3N_4 interlayer: (a) on Si substrate, (b) on Si_3N_4 interlayer.



Fig. 3. Differentiated stress-temperature evolution curves for the TiNi films with different Ti/Ni ratios on both Si substrate and Si_3N_4 interlayer: (a) on Si substrate, (b) on Si_3N_4 interlayer.

(avoid overlapping). Generally, during heating, there is one-150stage transformation from martensite to austenite, while 151during cooling, a two-stage transformation (i.e., austenite-152R-phase-martensite) can be observed. There is one excep-153tion for the Ni-rich film, and there seems a two-stage 154transformation during both heating and cooling, correspond-155ing to transformations among martensite, R-phase and 156austenite. Two-stage transformation behavior in TiNi films, 157especially for Ni rich films has been studied by many 158researchers, and it can be attributed to the fine internal 159

Tai	ble	2
		_

TICLE IN PR

Y. Fu et al. / Thin Solid Films xx (2004) xxx-xxx

Comparison of stress values of different TiNi films on different substrate obtained from wafer curvature measurement

obtained from wafer curvature measurement					
TiNi films		Residual stress (MPa)	Recovery stress (MPa)	Stress increase rate (MPa)	
On Si	Ti48.4Ni	161.3	201.5	8.35	
	Ti50.2Ni	11.3	376.4	25.35	
	Ti52.5Ni	95.9	272	15.45	
On Si ₃ N ₄	Ti48.4Ni	44.1	211.6	8.9	
	Ti50.2Ni	14.0	374.3	25.5	
	Ti52.5Ni	91.5	286.7	15.7	

t2.1

ARTICLE IN PRESS

Y. Fu et al. / Thin Solid Films xx (2004) xxx-xxx

t3.1 Table 3t3.2 Phase transformation temperatures obtained from stress evolution

		*					
TiNi films		А _s (К)	А _f (К)	R _s (K)	<i>R</i> _f (K)	М _s (К)	<i>М</i> _f (К)
On Si	Ti48.4Ni	311	338	329	309	_	_
	Ti50.2Ni	349	361	345	340	311	298
	Ti52.5Ni	337	352	330	324	_	_
On Si ₃ N ₄	Ti48.4Ni	329	342	324	311	305	_
	Ti50.2Ni	351	366	347	340	322	306
	Ti52.5Ni	347	365	345	337	_	_

160 structure, non-uniform stress distributions, and/or precip-161 itates, such as Ti_3Ni_4 , or Ti_2Ni , etc. [6,14,15].

162Results of film residual stress (i.e., the film stress at room temperature of 293 K) are listed in Table 2. The residual 163stress values are the lowest for the near-equiatomic samples 164165on both Si substrate and Si₃N₄ interlayer, due to the significant release of thermal stress caused by shape memory 166 167 effect as shown in Fig. 2. The difference in residual stress for films with different Ti contents can be explained from the 168 169differences in phase transformation behavior (see Fig. 2), intrinsic stress in the films, and/or precipitates in the films 170171[16]. Table 2 also lists recovery stress values (driving force for actuation) of the films, which is the difference between 172173 the maximum and minimum stress. The recovery stress values are the highest for Ti50.2Ni films, regardless of the 174 175existence of Si₃N₄ layer, indicating its actuation force is the 176maximum. The recovery stress values for TiNi films with and without Si₃N₄ layer are almost the same, probably 177because the silicon nitride layer is too thin to cause any 178significant influence on thermal stress and recovery stress. 179Table 2 lists the maximum stress increase rate during heating, 180 181 corresponding to actuation speed for the films on two types 182of substrates. The Ti50.2Ni film shows the highest value 183 indicating that the actuation speed is the maximum for this film during heating. There is little difference in the maximum 184increase rate for the films on Si substrate or Si₃N₄ interlayer. 185186The transformation temperatures for the TiNi films on two 187 substrates can be obtained from Fig. 2 or Fig. 3, and the 188results are summarized in Table 3. The transformation temperatures are the highest for near-equiatomic films 189



Fig. 5. Atomic element distribution into TiNi film interface peeled off from Si substrate.

regardless of substrates of different interlayers, which agrees 190 well with those of bulk TiNi materials [3,6]. 191

The critical loads obtained from scratch tests for the films 192on both Si substrate and Si₃N₄ interlayers are presented in 193Fig. 4. The critical load increases slightly with Ti content for 194all the films. For the Ti-rich films, the increased power of 195the Ti target will introduce more Ti to be sputtered at the 196interface, thus the adhesion could be slightly improved. 197From Fig. 4, it can also be concluded that introduction of 198Si₃N₄ layer has no apparent influence on the film adhesion 199properties. If compared with poor adhesion results of TiNi 200films on SiO₂ interlayer [10], Si₃N₄ interlayer seems a good 201choice for an electrically insulating and diffusion barrier 202layer in respect of adhesion properties. 203

The atomic concentration evolution from the peeled 204interface into Ti50.2Ni film on Si substrate is shown in Fig. 2055. The profiles show three different regions. The first region 206is C and O contamination layer with a few nanometers thick. 207The second region presents Si diffusion layer (about 30-40 208nm thick), and the last one is the bulk TiNi film. Results 209indicate that there is significant interdiffusion of Si atoms 210into TiNi films, and traces of silicon can be detected 40 nm 211beneath surface. Fig. 6 shows the atomic concentration 212changes of different elements from the peeled Si₃N₄ 213interlayer into TiNi film. The profile shows four different 214



Fig. 4. The critical loads obtained from scratch tests for the films on both Si substrate and Si_3N_4 interlayers.



Fig. 6. Atomic element distribution into TiNi film interface peeled off from $\rm Si_3N_4$ interlayer.

4

ARTICLE IN PRESS

Y. Fu et al. / Thin Solid Films xx (2004) xxx-xxx



Fig. 7. Ni 2p core level spectrum evolution with depth for Ti50.2Ni film deposited on Si_3N_4 interlayer.

215 regions. The first region is C and O contamination layer less 216 than 15 nm thick. The second region seems a thin Si_3N_4 217 layer about 50-80 nm thick. Results revealed that the peeled 218interface is actually in the silicon nitride side near the TiNi/ Si₃N₄ interface. The third region is the interdiffusion layer 219about 140 nm thick between Si₃N₄ layer and TiNi film. The 220intermixing layer is quite large compared with 120 nm for 221TiNi/Si system and 30 nm for TiNi/SiO₂ system [10]. High 222223content of nitrogen can be found throughout the interlayer 224indicating the significant diffusion of nitrogen. Ti content increases rapidly, and high Ti content is dominant through-225226out the interlayer. Silicon content decreases significantly, 227and then remains a low content afterwards. The fourth 228region is the TiNi bulk film.

Fig. 7 shows Ni 2p core level spectra evolution with 229230depth for TiNi/silicon nitride interlayer. On the surface, there is no Ni peak found. After Ar ion sputtering away 80 231nm, weak peaks of Ni can be found. The intensities of Ni 232peaks gradually increase with depth. Ni mainly exists in the 233 234metallic state with broad satellite peaks due to sputter-235damaged crystallites [10], and no significant shift for the Ni 2p peak with depth is observed. 236

Fig. 8 shows Ti 2p spectra evolution with depth. On the surface, there is no Ti peak detected. Weak peaks of Ti can be found after sputtering away 80 nm, and then Ti peak



Fig. 9. Si 2p core level spectrum evolution with depth for Ti50.2Ni film deposited on Si_3N_4 interlayer.

intensities rapidly increase with depth. Ti-N bond is 240dominant near the film surface, with small amount of Ti-241 O bond. The binding energies of Ti-N bonds are relatively 242larger than those of metallic Ti in TiNi phase, indicating a 243charge transfer caused by the TiN formation. The N in Ti-N 244bonds actually came from the decomposition of Si₃N₄ phase 245and diffusion of nitrogen element. The results revealed that 246there is significant interdiffusion and reaction between Ti 247elements in TiNi film and N in Si₃N₄ layer. After further 248sputtering, Ti 2p peaks in Ti-N bonds gradually shift to 249lower binding energy of metallic Ti bonds (corresponding to 250TiNi) as shown in Fig. 8. The broad shoulders near Ti 2p 251peak can be attributed to satellite structures [10]. Beneath 252this layer, Ti mainly exists in metallic state. 253

Fig. 9 shows the evolution of Si 2p spectrum with depth. 254At the surface, Si-O bond (SiO₂) is dominant. With the 255increase of depth, there is a dramatic increase in Si-N bonds 256and decrease in Si-O bond. The dominance of Si-N bonds 257extends 80 nm. Further into films, pure Si-Si bond can be 258detected and become dominant in Si 2p spectra, although 259both Si-N and Si-Si bonds are relatively weak. The 260formation of pure Si is attributed to the interdiffusion and 261reaction of Ti with N in Si₃N₄ bonds. Further into the TiNi 262film, silicon bonds gradually disappear. 263

Fig. 10 shows the N 1s core level XPS spectra evolution 264 into the peeled TiNi films. Nitrogen content is quite high at 265



Fig. 8. Ti 2p core level spectrum evolution with depth for Ti50.2Ni film deposited on Si_3N_4 interlayer.



Fig. 10. N1s core level spectrum evolution with depth for Ti50.2Ni film deposited on Si_3N_4 interlayer.

6

ARTICLE IN PRESS

Y. Fu et al. / Thin Solid Films xx (2004) xxx-xxx

266 the peeled surface, and the main features can be assigned as 267 N–Si (397.2 eV) [17], corresponding to Si_3N_4 . With the 268 increase of depth into film, there seems a minor shift of N 1s 269 peak to lower binding energy, which is from the contribu-270 tion of N–Ti bond (396.5 eV). Near to TiNi bulk film, N 271 peak gradually decreases and finally disappears. N1s spectra 272 evolution can also reveal the formation of Ti–N bond due to 273 the element interdiffusion.

274 In brief, results showed that the addition of Si_3N_4 275 interlayer between film and Si substrate did not cause much 276 change in phase transformation behavior as well as adhesion

277 properties, and XPS analysis showed clearly the significant

278 interdiffusion of elements and formation of Ti-N and pure

279 Si-Si bonds at the Si₃N₄/TiNi interlayer.

280 4. Conclusions

281Near-equiatomic TiNi films were found to have the 282lowest residual stress and the highest recovery stress 283regardless of the existence of Si₃N₄ interlayer. The addition 284of Si₃N₄ interlayer between film and Si substrate did not 285cause much change in phase transformation behavior as well as adhesion properties. XPS analysis revealed that at the 286287 TiNi film/Si₃N₄ interlayer, there is significant interdiffusion 288 of elements, formation of Ti-N bonds, and pure Si-Si 289 bonds. Scratch test results showed that adhesion between 320

the TiNi film and substrate was slightly improved with the 290 increase of Ti content in TiNi films. 291

292

293

295

296

298

299

300

303

304

305

306

307

308

309

310

311

312

References

- [1] K. Otsuka, X. Ren, Intermetallics 7 (1999) 511. 294
- [2] J.V. Humbeeck, Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process. 273–275 (1999) 134.
- [3] Z.G. Wei, R. Sandstorm, S. Miyazaki, J. Mater. Sci. 33 (1998) 3743. 297
- [4] A. Ishida, V. Martynov, MRS Bull. 27 (2002) 111.
- [5] P. Krulevitch, A.P. Lee, P.B. Ramsey, J.C. Trevino, J. Hamilton, M.A.M.A. Northrup, J. MEMS 5 (1996) 270.
- [6] S. Miyazaki, A. Ishida, Mater. Sci. Eng., A Struct. Mater.: Prop. 301 Microstruct. Process. 273–275 (1999) 106. 302
- [7] R.H. Wolf, A.H. Heuer, J. MEMS 4 (1995) 206.
- [8] Y.Q. Fu, H.J. Du, W.M. Huang, S. Zhang, M. Hu, Sens. Actuators, A, Phys. 112 (2004) 395.
- [9] H. Kahn, M.A. Huff, A.H. Heuer, J. Micromechanics Microengineering 8 (1998) 213.
- [10] Y.Q. Fu, H.J. Du, S. Zhang, Thin Solid Films 444 (2003) 88.
- [11] S. Stemmer, G. Duscher, C. Scheu, A.H. Heuer, M. Ruhle, J. Mater. Res. 12 (1997) 1734.
- [12] Y.Q. Fu, H.J. Du, Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process. 342 (2003) 236.
- [13] Y.Q. Fu, H.J. Du, S. Zhang, Surf. Coat. Technol. 153 (2002) 100. 313
- T. Lehnert, S. Tixier, P. Boni, R. Gotthardt, Mater. Sci. Eng., A Struct. 314
 Mater.: Prop. Microstruct. Process. 273–275 (1999) 713. 315
- [15] H. Rosner, A.V. Shelyakov, A.M. Glezer, P. Schlobmacher, Mater. Sci.
 Eng., A Struct. Mater.: Prop. Microstruct. Process. 307 (2001) 188.
 317
- [16] Y.Q. Fu, H.J. Du, S. Zhang, Surf. Coat. Technol. 167 (2003) 120. 318
- [17] J. Kovac, G. Scarel, M. Sancrotti, J. Appl. Phys. 86 (1999) 5566. 319