The Influence of an OTS Self Assembled Monolayer on the Wear Resistant Properties of Polysilicon Based MEMS

M.A.Baker^{}, J.Li*

The Surface Analysis Laboratory, School of Engineering, University of Surrey,
Guildford, Surrey, GU2 7XH, UK

Abstract

Polysilicon MEMS structures are coated with self-assembled monolayers (SAMs) to reduce stiction and improve wear resistance. This study reports on an octadecyltrichlorosilane (OTS) coated low pressure chemical vapour deposited (LPCVD) polysilicon based MEMS test structure fabricated at Sandia National Laboratories, USA. The surface morphology and OTS layer have been studied by SEM, XPS and AFM. Nanowear properties were investigated using a diamond tipped cantilever AFM. The presence of OTS is confirmed by XPS and AFM measurements and the polysilicon/OTS interface is found to be vulnerable to hydrolysis when stored under laboratory conditions. A comparison is made between the wear resistance of the OTS coated and uncoated surfaces of the MEMS polysilicon components and silicon nitride substrate. Nanowear

results were also obtained for CVD polysilicon and silicon nitride layers and a silicon wafer. The presence of the OTS layer was found to enhance the wear properties of the MEMS polysilicon and silicon nitride layers, with an increase in the wear resistance of up to 2 times for the MEMS polysilicon and up to 3 times for the MEMS silicon nitride.

Keywords: MEMS, wear, XPS, AFM

1. Introduction

Silicon and other electronic materials are being used to fabricate devices which can perform mechanical operations. Using standard integrated circuit (IC) processes, namely layer deposition, doping, lithography and etching, together with special etching and bonding procedures, three dimensional microstructures can be generated. The combination of individual components such as motors, actuators and gears, enables the fabrication of micromachines [1]. Polysilicon deposited by low pressure chemical vapour deposition (LPCVD) is a well-known material in standard IC technologies and suitable for fabrication of micromechanical structures. Polysilicon is thus employed as the structural material and silicon nitride as the isolation layer.

Due to the high surface area to volume ratio, the mechanical microstructures are vulnerable to adhesion upon contact, a phenomenon commonly known as stiction. For MEMS, there are generally two stiction related phenomena, release-related stiction and

in-use stiction. In-use stiction occurs during operation, when microstructure surfaces come into contact. If adhesive interactions exceed restoring forces, the surfaces will not separate, causing device failure. Self-assembled monolayers (SAMs) are widely used to reduce release-related stiction in MEMS fabrication. The effect of SAMs on friction and wear of Si based layers has been studied in detail by Bhushan and co-workers [e.g. 2,3]. On working Si based MEMS devices, alkylsilane SAMs have been shown to reduce wear by approximately a factor of 2 for end stopper test structures [4] and octadecyltrichlorosilane $C_{18}H_{37}SiCl_3$ (OTS) has proven wear resistant properties on polysilicon motors [5]. In this work, the surface chemistry and wear resistance of polysilicon MEMS test structures coated with OTS are investigated using XPS and AFM. A comparison is made between the properties of a MEMS polysilicon gear (OTS coated and uncoated), the MEMS silicon nitride substrate (OTS coated and uncoated), CVD polysilicon and silicon nitride layers and an uncoated silicon (100) wafer.

2. Experimental

An OTS coated polysilicon MEMS test structure, consisting of electrostatic motors, gears and actuators was fabricated at the Sandia National laboratory, USA. Details of the OTS treatment are given in [6]. XPS spectra were recorded from a Thermo VG Scientific Sigma-Probe spectrometer using a monochromated Al $K\alpha$ source (140 W) and employing a spherical sector analyser. Spectra were recorded from an area of $250\ \mu m^2$ and at a take-off angle of 37° with respect to the sample surface. Survey spectra were taken at a pass energy of 150 eV and elemental narrow scans at 20 eV (0.1 eV step).

Peaks were curve fitted using a mixed Gaussian/Lorentzian function after a Shirley background subtraction and quantification performed using instrument modified Wagner sensitivity factors. Peak fits were performed with a ± 0.2 eV constraint on the component binding energies. A Nanoscope III, Digital Instruments AFM was used to investigate morphology and undertake nanowear studies. For both morphological and wear measurements, a three-sided pyramidal natural diamond tip mounted on a gold coated stainless steel cantilever beam (spring constant 160 N/m) was employed. The diamond has an apex angle of 80° and a tip radius of about 120 nm (measured by using SEM). Specimens were scanned orthogonal to the long axis of the cantilever with a scanning speed of 1 $\mu\text{m/s}$ at various loads to generate wear marks. In order to observe the wear marks and measure their depth, a larger sample surface area was scanned before and after the nanowear test using the same diamond tip at a normal load of 500 nN. The reported wear depths are an average of three measurements. SEM images of the MEMS was obtained with a field emission Hitachi S-4000 SEM at a primary beam energy of 10 keV.

3. Results

3.1. OTS layer

An SEM image of the gear mechanism used to drive an actuator on the MEMS device is shown in Figure 1. The gears have diameters ranging from about 80 – 400 μm . AFM force-displacement curves, shown in Fig. 2, provide information on the hydrophobicity of the different surfaces. From these curves, the area given by the negative part of the withdrawl curve (defined by the crosses, x) in Fig 2 (a) is directly proportional to the

work of adhesion between the sample surface and the AFM tip. If both the tip and sample surface are hydrophilic, there will be a strong adhesive interaction between them and this area will be large. However, if one of the surfaces is hydrophobic, the adhesive interaction will be reduced. The AFM tip used here is silicon, which is hydrophilic. The large areas of the force-displacement curves for the Si (100) wafer and CVD silicon nitride layer indicate that both of these surfaces are hydrophilic. A much lower adhesive interaction is found for the MEMS polysilicon gear and silicon nitride substrate surfaces, indicating that both are hydrophobic. These results provide strong evidence for the presence of the OTS monolayer on the MEMS surface. The XPS Si 2p and C 1s spectra have been presented previously [7] and the results are also supportive of OTS being present on the MEMS surface.

In Fig. 3, XPS spectra of the MEMS polysilicon gear taken soon after receiving the samples and then after 7 months storage in air are presented. The Si 2p peak of an air-oxidised silicon surface can be fitted into 5 components, corresponding to elemental Si, Si₂O, SiO, Si₂O₃ and SiO₂ at 99.5, 100.4, 101.4, 102.0 and 102.8-104.3 eV respectively according to Seah and Spencer [8]. For the OTS coated MEMS polysilicon, an additional R-SiO₃ functionality is also present with a binding energy of approximately 102.9 eV [9]. This peak will contribute to the SiO₂ component in the peak fit. The most dominant components found from the peak fit were Si₂O, Si₂O₃ and SiO₂ + R-SiO₃. The spectrum is very similar to that presented by Ashurst et al for an OTS coated Si (100) surface [10]. The presence of various silicon oxide peaks in addition to the R-SiO₃ peak is indicative of some oxidation of the underlying silicon. This is further supported by the increased

intensity of the oxide peak after 7 months of air exposure. The susceptibility of the OTS Si-O-Si bonds (at the SAM/Si interface) to hydrolysis has previously been noted at high humidities [11] and these results demonstrate that this vulnerability exists even under normal laboratory storage conditions.

3.2. Wear

To provide information on the effectiveness of OTS in reducing wear, a comparison of the wear properties of the MEMS with and without the SAM layer is required.

Consequently, the OTS layer needs to be removed from the MEMS surface. This was achieved by bombarding the surface with a Ga^+ ion beam in a VG Reflectron ToF-SIMS using an accelerating voltage of 15 keV and 5 nA specimen current. The surface was etched until no presence of the OTS layer remained.

Figure 4 shows AFM images of wear scars created on the OTS coated and uncoated MEMS polysilicon gear and silicon nitride substrate surfaces using a 50 μN normal load. The wear scars are the result of a single scan on the polysilicon gear and five scans on the harder silicon nitride substrate. The improved wear resistance offered by the OTS coating is evident. To study the wear behaviour of the MEMS materials, both coated and uncoated over a range of different conditions, nanowear tests were undertaken at normal loads ranging from 10 – 80 μN and comparison was made with reference samples (Si (100) wafer, LPCVD polysilicon and CVD silicon nitride layers). The results are shown in Figure 5.

For the silicon samples (Fig. 5 (a)), wear of all surfaces is similar up to 35 μN . Above 35 μN , the Si wafer undergoes severe wear. Analysis of wear debris shows this to be a result of cutting wear [11]. The polysilicon surfaces exhibit a much stronger resistance to wear at higher loads, due to the smaller grain size in these materials. The difference between the LPCVD polysilicon layer and MEMS gear is probably due to a variation in the dopants, dopant concentrations or CVD process parameters used to fabricate the two layers. Most importantly, over the load range, the behavioural trend between the OTS coated and uncoated MEMS is similar and the former displays an improvement in the wear resistance by approximately a factor of two. Similar data was obtained by Liu and Bhushan for polysilicon coated with a 4,4-dihydroxybiphenyl SAM layer [2].

The silicon nitride layers (Fig. 5 (b)), show a much higher wear resistance than polysilicon. At 60 μN , approximately a thirteen times improvement in wear resistance is observed for the uncoated MEMS silicon nitride compared to uncoated MEMS polysilicon. This can be attributed to the covalently bonded silicon nitride layers having a high hardness and a microstructure resistant to cutting wear [12]. The CVD silicon nitride layer and uncoated MEMS substrate show the same wear dependence on normal load. Coating the MEMS silicon nitride with OTS leads to an improvement in the wear resistance at all loads in the range 20 – 80 μN . An increase in wear resistance of approximately a factor of three is observed at loads of 60 – 70 μN .

4. Discussion

The beneficial effect of OTS on wear resistance is apparent for both polysilicon and silicon nitride substrates. Liu and Bhushan have described that during wear of SAM coated substrates, a 'critical load' exists, above which the monolayer is removed from the surface [2]. However, our results show that OTS offers enhanced wear resistance over a wide load range, including loads above the 'critical load'. Consequently, the monolayer is having a beneficial effect even when the AFM tip penetrates through the monolayer and into the substrate. In this situation, rather than serving as a protective surface layer, OTS molecules can only reduce wear by acting to reduce friction between the tip and substrate. During wear at high loads, the SAMs will be removed from the surface and may remain intact or be broken into fragments. It is proposed that the detached molecules and fragments adhere to both surfaces forming an interfacial lubricating tribo-layer which acts to lower friction at the interface.

The OTS coating improves the wear resistance of silicon nitride more than polysilicon (Figure 5). A possible explanation for this is the different wear mechanisms operating on the two materials. Li has shown that the wear mechanisms for the materials examined here are cutting wear for the Si (100) wafer, brittle fracture for silicon nitride and a mixed cutting/fracture process for polysilicon [12]. In a cutting process, compared to brittle fracture, the tip is in almost constant contact with the substrate and the molecules have difficulty in gaining access to the interface. Consequently, for polysilicon there is less opportunity for SAMs to lubricate.

The XPS results presented in Figure 3 have shown that SAM/substrate interfacial bonding on polysilicon is being weakened by hydrolysis. However, the Si 2p peak of the MEMS silicon nitride was unchanged after 7 months air exposure, indicative of a stable interface. Maboudian has found that good quality OTS monolayers can be grown on silicon nitride due to the polar nature of the surface and the formation of a water overlayer in ambient conditions [13]. Compared to SiO₂, the reduced number of silanol bonding sites on the silicon nitride surface [13] may promote the formation of dense, well-ordered and highly cross-linked OTS layers [14] offering a stronger resistance to water penetration than OTS layers formed on polysilicon. The greater stability of the monolayer gives rise to improved wear resistance properties for silicon nitride.

5. Conclusions

- (i) OTS improves the wear resistance of MEMS polysilicon (by up to a factor of two) and silicon nitride (by up to a factor of three) over the load range 20 – 70 μN .
- (ii) The OTS coated polysilicon MEMS is subject to hydrolysis of the SAM/substrate interface.
- (iii) The enhanced performance of the OTS coating on MEMS silicon nitride compared to polysilicon can be attributed to the formation of a denser, more hydrolysis resistant monolayer at low loads and a greater capacity for lubrication during wear of silicon nitride at high loads.

References

- [1] Linder C, Paratle L, Gretillat MA, Jaecklin VP, Rooij NF. *J. Micromech. MicroEng.* 1992; **2**: 122
- [2] Liu H, Bhushan B. *Ultramicroscopy* 2002; **91**: 185
- [3] Bhushan B, Israelachvili JN, Landman U. *Nature* 1995; **374**: 607
- [4] Åström R, Mutikainen R, Kuisma H, Hakola A-H. *Wear* 2002; **253**: 739
- [5] Deng K, Collins RJ, Mehregany M, Sukenik CN. *J. Electrochem. Soc.* 1995; **142**: 1278
- [6] Srinivasan U, Houston MR, Howe RT, Maboudian R. *J. Microelectromechanical Systems* 1998; **7**: 252
- [7] Li J, Cui Z, Baker MA. *Surf. Interface Anal.* 2004; **36**: 1254
- [8] Seah MP, Spencer SJ. *Surf. Interface Anal.* 2003; **35**: 515
- [9] Alexander MR, Short RD, Jones FR, Michaeli W, Blomfield CJ. *Appl. Surf. Sci.* 1999; **137**: 179
- [10] Ashurst WR, Yau C, Carraro C, Lee C, Kluth GJ, Howe RT, Maboudian R. *Sensors and Actuators A* 2001; **91**: 239
- [11] Angst DL, Simmons GW. *Langmuir* 1991; **7**: 2236
- [12] Li J. PhD Thesis, University of Surrey, UK. 2005
- [13] Maboudian R. *Surface Science Reports* 1998; **30**: 207
- [14] Wang MJ, Liechti KM, Wang Q, White JM. *Langmuir* 2005; **21**: 1848

Figure Captions

- Figure 1: SEM image of MEMS gears (polysilicon) and substrate (silicon nitride).
- Figure 2: AFM force-displacement curves for a Si (100) wafer, CVD silicon nitride layer, MEMS polysilicon gear and MEMS silicon nitride substrate.
- Figure 3: XPS Si 2p spectra for the OTS coated MEMS polysilicon gear (a) as-received; (b) after 7 months storage in air.
- Figure 4: AFM images of wear scars on (a) MEMS polysilicon gear: OTS coated (left) and uncoated (right); (b) MEMS silicon nitride substrate: OTS coated (left); uncoated (right). AFM tip parameters – 50 μ N normal load, polysilicon 1 cycle, silicon nitride 5 cycles.
- Figure 5: Wear depth as a function of normal load for (a) polysilicon MEMS gear (uncoated and OTS coated), CVD polysilicon layer and Si (100) wafer; (b) silicon nitride MEMS substrate (uncoated and OTS coated) and CVD silicon

nitride layer