

WTC2005-63573

Surface Treatments for Modifying the Tribological Behavior of Microsystems

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ABSTRACT

The surfaces of microelectromechanical systems (MEMS) that have impacting and sliding contacts are frequently modified by coatings to improve the tribological behavior of the structural material. In silicon microsystems, chemisorbed hydrocarbon or fluorocarbon monolayers are commonly used to modify the surface energy of the oxidized silicon to resist water adsorption and adhesion. Thin conformal solid films can also be employed to improve the wear resistance of the structural material. The requirements of coatings for microsystems will be discussed in terms of tribological behavior, processing, operation and aging characteristics. Although contacting surfaces of polycrystalline silicon have arithmetic roughness of less than 50 nm, contact forces below 1 mN prescribe that real contact occurs at only a few asperities. Defects in the coatings, and interfaces that are deeply buried present opportunities for adsorption of reactive species and degradation of the coating over time. An understanding of the mechanical and chemical degradation mechanisms of tribological coatings is of primary importance for the reliable operation of microsystems. At the same time, relating composition and structure of the contacting surfaces to the tribological behavior is quite challenging due to the limited size and number of real contact spots. A variety of surface treatments for silicon microsystems have been investigated, including chemisorbed monolayers, vapor phase lubricants and hard coatings. The tribological behavior of polycrystalline silicon containing chemisorbed monolayers is dramatically influenced by water vapor in the environment during fabrication processes, storage or operation. Surface analytical tools and friction measurements using micromachined tribometers to understand the impact of coating degradation on the tribological behavior of microsystems are illustrated.

INTRODUCTION

MEMS surfaces have morphology that is defined by the processes used to grow the structural layer and the etch used to pattern this layer. In the case of polycrystalline silicon devices, the planar surfaces are influenced by the nucleation and growth of polycrystalline silicon on oxide sacrificial layers. Sidewall surfaces are created by the plasma etch used to pattern this film to create devices. Atomic Force Microscope (AFM) images of planar and sidewall surfaces of polycrystalline silicon structures are shown in Figure 1. Apparent contact areas between MEMS structures are usually on the order of $2 \times 2 \mu\text{m}$. At forces below 1 mN, there will be only one to several points of real contact.

Surface treatments for microsystems must withstand exposure to temperatures and environments associated with back-end-of-line processes such as packaging, as well as operational conditions that may involve cryogenic as well as elevated temperatures. Reactions of the solid surfaces at real points of contact with species inside the package environment will lead to changes in the adhesion and friction behavior of the interface. Chemisorbed monolayers, as well as solid lubricant and hard coatings, have been investigated in terms of coverage on buried interfaces, tribological behavior, and aging characteristics.

MONOLAYER COVERAGE

Chemisorbed monolayers such as alkyl- or amino-silanes have been used to reduce the surface energy of polycrystalline silicon, thereby reducing adhesion and friction forces at real points of contact [Mastrangelo, 1997; Maboudian et al., 2000]. Coupling agents applied to silicon MEMS consist of a functional group designed to bond to the silicon surface, and a terminal group with good chemical stability and low surface

energy. They may be applied from solvent solution or in the vapor phase [Mayer et al., 2000], and given sufficient deposition time are envisioned to coat the surface to one monolayer thickness in a conformal layer, penetrating narrow gaps. In order to examine the coverage of chemisorbed monolayers on silicon MEMS structures having hidden surfaces, a flap structure was developed, as shown in Figure 2. The flap is fabricated, released and coated in the “closed” position, creating a gap of 1.5 μm between the flap and the silicon substrate due to the large dimples under the flap. The flap can then be flipped over and latched in position to expose the hidden interface for analysis.

Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) is the tool of choice for examining MEMS surfaces since it combines adequate spatial resolution ($\sim 0.5 \mu\text{m}$) with high surface sensitivity and information on the chemical state of surface species. However, the ion spectra resulting from analysis of a monolayer coated polycrystalline silicon surface is rich in information, with a peak at almost every mass. Therefore, a multivariate analysis algorithm was used to process the ion spectra [Ohlhausen et al., 2004]. Briefly, a full spectrum is acquired at every pixel in an ion image, and the ion spectra with associated spatial coordinates are processed using the algorithm to extract the fewest spectra that represent all ion spectra in the image, along with intensity maps representing the concentration of each component in the analysis area. A typical result is shown in Figure 3 for perfluorodecyltrichlorosilane ($\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{SiCl}_3$, FDTS) deposited from 1 mM solution in hexadecane. Ellipsometry shows that steady-state coverage is achieved within a few hours, but this sample was kept in the coating solution for 16 hours. Analysis of the SIMS data revealed a single component associated with the monolayer, and that the concentration of this component is reduced in the hidden area. Boxes on the image show locations where the intensity of this component was calculated, and indicate that the hidden surface has 40% of the concentration of FDTS that is present on the exposed surface. These hidden areas are representative of many contact interfaces in MEMS, and understanding the impact of monolayer degradation on tribological behavior requires examination of these areas.

MONOLAYER DEGRADATION

Hydrolysis of chemisorbed monolayers for MEMS is known to occur at temperatures above 100°C [Srinivasan et al., 1998] resulting in increased surface energy. Dugger et al. [2003] recently showed that hydrolysis occurs at water vapor concentrations below 5000 ppmv (13% RH), that the reduction in surface energy corresponds to reduced concentration of the monolayer, and that the static friction coefficient between MEMS surfaces increased from 0.12 to 0.23 as a result.

Spectral imaging and SIMS analysis has been used to investigate hydrolysis of a vapor-deposited aminosilane ($\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{N}(\text{CH}_3)_2)_3$, perfluoro-octyltris(dimethylamino)silane) on silicon MEMS surfaces. Figure 4 shows the spatial distribution for the two components identified. The components are designated “low mass” and “high mass” due to differences in concentrations of mass fragments in the two components. The spectral images show that the low mass component is preferentially located in the hidden areas, while the high mass component is depleted in these areas. The mechanism responsible for the observed differences in fragmentation of the molecule depending on location is still under investigation. The spectral images for the sample exposed to 2000 ppmv H_2O in N_2 at 300°C shows a significant reduction in the concentration of the high mass component, and increase in the low mass component.

CONCLUSION

Contact between MEMS structures occurs at just one to several points in the apparent area of contact, given the morphology, applied forces and size of apparent contact surfaces. Chemical reactions between surface treatments and species in the environment at these points of contact will govern the adhesion and friction behavior of MEMS structures. Multivariate analysis of TOF-SIMS spectra have shown that chemisorbed monolayers are not uniformly distributed on hidden and exposed areas, and can be used to determine the relative reduction in concentration of monolayers due to hydrolysis reactions. The application of other coatings to microsystems, including wear-resistant layers and solid lubricants, will be discussed. The use of micromachined tribometers to investigate coating performance and degradation will be illustrated.

ACKNOWLEDGMENTS

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

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FIGURES

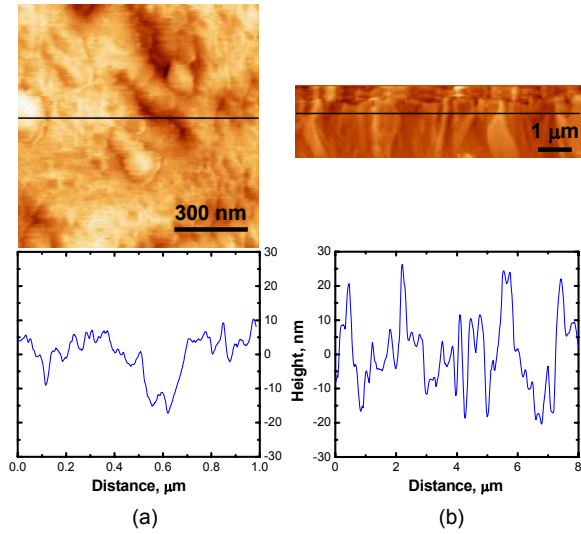


Figure 1. AFM images and profiles for planar (a) and sidewall (b) polycrystalline silicon MEMS surfaces.

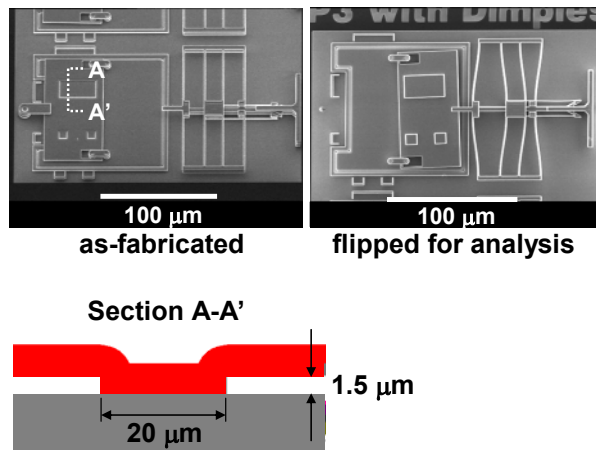


Figure 2. Polycrystalline silicon flap structure for investigating monolayer coverage on hidden surfaces.

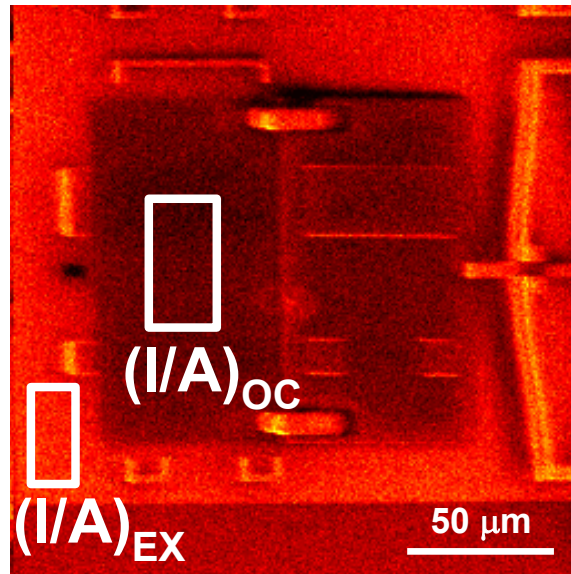


Figure 3. Spectral image of FDTS concentration on a MEMS flap that has been flipped over.

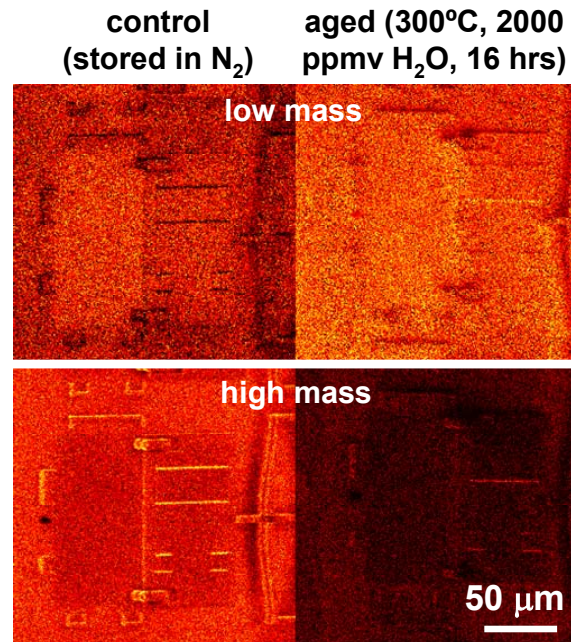


Figure 4. Spectral image of control and aged flaps coated with FOTAS and flipped over.