NANODYNAMICS OF VAPOR-PHASE ORGANOPHOSPHATES ON SILICON AND OTS FOR MEMS LUBRICATION PURPOSES

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ABSTRACT
We have performed a quartz crystal microbalance (QCM) study of the nanotribological properties of organophosphate (tricresylphosphate and t-butyl phenylphosphate) layers adsorbed from the vapor phase onto silicon (amorphous silicon and MEMS-like polysilicon), and octadecyltrichlorosilane (OTS) treated silicon and gold surfaces. The latter systems have been studied in order to explore whether organophosphates and OTS in combination might prove synergistic from a tribological point of view [1]. There is a strong possibility that this combination will also exhibit synergistic tribological behaviors when tested on actual MEMS devices. Therefore, it is important to perform QCM measurement on silicon that is as close to that of MEMS devices. In order to perform this study, we have developed a deposition method involving a Si-Ge layer that enables the growth of polycrystalline silicon on top of Cu QCM electrodes. The structural and morphological properties of these samples have been characterized with Raman spectroscopy and atomic force microscopy (AFM), confirming that they are similar in nature to the silicon in actual MEMS devices.

1. INTRODUCTION
MEMS devices are highly susceptible to surface forces that can cause suspended members to deflect towards the substrate, collapse and/or adhere permanently to the substrate. A number of surface treatments have met with varying degrees of success for alleviation of MEMS-related stiction/adhesion problems, but the wear attributes and durability of surfaces in sliding or intermittent contact remains problematic [2]. Tribological issues have thus emerged as the limiting factors in the development and commercialization of a wide variety of MEMS devices, with surface treatments being the weakest link in overall system reliability and performance.

OTS (octadecyltrichlorosilane) layers have received much attention as anti-stiction treatments for silicon MEMS devices, but are not particularly wear resistant, and decompose at 450°C (in vacuum) or lower, depending upon the environment. Tricresylphosphate (TCP) and t-butyl phenyl phosphate (TBBP) are vapor phase organophosphates that are highly effective in preventing wear and oxidation for high temperature for macroscopic applications [4]. They were first suggested for MEMS applications in 1992, but whether they could effectively lubricate MEMS structural materials such as silicon and/or OTS treated silicon, or even adsorb in significant quantities on them was subsequently never investigated. Neeyakorn et. al. recently reported a set of QCM measurements of the mobility and self-healing nature of bound-plus-mobile lubricants for MEMS applications. In particular, the nanotribological properties of organophosphate (trycresylphosphate and t-butyl phenyl phosphate) layers adsorbed from the vapor phase onto both amorphous silicon, and octadecyltrichlorosilane (OTS) treated silicon and gold surfaces. The majority of the systems studied were observed to exhibit interfacial slippage and/or viscoelasticity in response to the oscillatory motion of the QCM [1]. Such effects have been previously linked to beneficial tribological performance [3]. We report here how polycrystalline, rather than amorphous, silicon layers can be deposited on QCM electrodes. The goal is to perform QCM measurements on silicon that is as close to that of actual MEMS devices.

2. EXPERIMENTAL DETAILS
A quartz crystal microbalance (QCM) consists of a single crystal of quartz that oscillates in transverse shear motion with a quality factor $Q$ near $10^5$. Metal film electrodes evaporated onto its two major faces serve as the substrates for adsorption studies. The QCM technique is particularly well adapted for measurements of uptake rates of vapor-phase lubricants, providing a sensitive, real-time mean for monitoring mass
adsorption from the gas phase, and also tribological properties of the reaction film [3]. QCM is also an attractive technique for comparative studies of macroscopic and microscopic phenomena, owing to the high sliding speeds (up to 2 m/s) and shear rates at which the data are recorded.

Polished grade, 5 MHz, AT-cut (transverse shear mode) QCM crystals were employed for these studies, obtained from Maxtek Inc. with thin layers of silicon and/or Au/Cr metal already deposited onto both sides. The Si films, as prepared by Maxtek, Inc., consist of 1000 Ang. of 99.999% pure material deposited onto both crystal sides, each of which was preplated with 2900/400 Ang. thick Au/Cr underlayers.

We are also interested in performing QCM measurements on polycrystalline, rather than amorphous, silicon that is similar in nature to the silicon in actual MEMS devices. To obtain this MEMS-like polysilicon, silicon is deposited onto the Ti layers in nature to the silicon in actual MEMS devices. To obtain this on polycrystalline, rather than amorphous, silicon that is similar with 2900/400 Ang. thick Au/Cr underlayers.

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Therefore, depositing crystalline Si on top of a quartz crystal undergoes a phase change at the typical temperature for 573 °C. This was achieved by depositing Si onto Ti layers to a thickness of ~ 100 nm by solid source Si-Ge MBE. In figure 1a, our Raman Spectroscopy shows the sharp feature at 520 cm⁻¹ representing the triply degenerate zone center mode of crystalline silicon. The presence of crystalline silicon is confirmed by the intense peak located at 520 cm⁻¹.

Fig. 1 Raman Spectroscopy of a) a poly crystalline silicon film, and b) a film with an amorphous silicon component. (The peak at ~260 cm⁻¹ is a calibration line.)

As shown in Figure 1b, any disorganization in the polycrystalline silicon is recognized by the presence of relatively broad peaks around 150 and 480 cm⁻¹. These features correspond to the broadened density of vibrational states of the Si. The ratio intensities of ~520 and 480 cm⁻¹ peaks in the films can be employed to determine the relative fraction of amorphous silicon in a sample.

To confirm the morphology of Si surface, the AFM scans were obtained with an Autoprobe M5 AFM in contact mode, with scan dimensions of 20 µm x 20 µm. The scans clearly indicate a corrugated surface, with an rms roughness that varied between 8-20 nm, and average roughness that varied between 6-15 nm.

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REFERENCES

1. W. Neeyakorn, M. Varma, C. Jaye, C. Grant and J. Krim, “Nanodynamics of Vapor-Phase Organophosphates on Silicon and OTS for MEMS Lubrication Purposes” submitted to Tribology Letters

3. RESULTS AND DISCUSSION

From our previous study, we conclude that the organophosphate and organophosphate+OTS combinations that are slipping are all potential candidates for silicon MEMS systems [1]. There is a strong possibility that these combinations will exhibit synergistic tribological behaviors when tested on actual MEMS devices. Given the high degree of variability of the nanodynamical properties associated with the various silicon surfaces, the combination of an organophosphate + OTS appears most likely to provide desirable tribological properties. In addition, TBPP and TCP may well protect the OTS layer from environmental degradation at elevated temperatures since they are excellent high-temperature lubricants and antioxidant. Work is now in progress to do comparative QCM study on the crystalline silicon which is deposited on top of QCM crystal.

The deposition technique is developed in order to grow MEMS-like polycrystalline silicon on top of QCM electrodes. A crystalline quartz undergoes a phase change at the temperature of 573 °C and the typical temperature for polycrystalline silicon film deposition is 750 – 900 °C. Therefore, depositing crystalline Si on top of a quartz crystal must be done at a temperature lower than 573 °C. This was achieved by depositing Si onto Ti layers to a thickness of ~ 100 nm by solid source Si-Ge MBE. In figure 1a, our Raman Spectroscopy shows the sharp feature at 520 cm⁻¹ representing...