

Dynamics of Vapor-phase Organophosphates on Silicon and OTS

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Abstract We have performed a quartz crystal microbalance (QCM) study of the uptake and nanotribology of organophosphate (tricresylphosphate (TCP) and t-butyl phenyl phosphate (TBPP)) layers adsorbed from the vapor phase onto amorphous and polycrystalline silicon and octadecyltrichlorosilane (OTS) treated silicon substrates. The materials were selected for their relevance to MEMS applications. About 3–5 monolayer-thick organophosphate films are observed to form readily on both silicon and OTS-treated silicon. The coatings moreover exhibit mobility in the form of interfacial slippage or viscoelasticity in response to the oscillatory motion of the QCM, implying that enhanced tribological performance may be expected in MEMS applications.

Keywords Vapor Phase Lubricants · Friction · QCM · Nanotribology · SAMS · Silicon

Introduction

Micro-Electro-Mechanical Systems (MEMS) are an emerging, cutting-edge technology that relies on the microfabrication of small-scale mechanical components (actuators, sensors, mirrors, etc.) and the integration of those components with on-board electronic processing.

Since MEMS devices must react to mechanical signals, many employ construction topologies that require physical motion. Suspended plates and beams that are fabricated a few microns away from their supporting substrates are in common use. In addition, materials processing constraints frequently result in the fabrication of self-mated surfaces of like materials. These combined characteristics make MEMS devices highly susceptible to surface forces that can cause suspended members to deflect toward the substrate, collapse and/or adhere permanently to the substrate [1]. In particular, van der Waals and electrostatic forces at this scale become comparable or even larger than body forces such as gravitational, inertia, and capillarity in the face of suspension architectures having low compliance.

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.

Octadecyltrichlorosilane (OTS) layers have received much attention as anti-stiction treatments for silicon MEMS devices. They are not, however, particularly wear resistant, and decompose at 450 °C (in vacuum) or lower, depending upon the environment [3]. Tricresylphosphate (TCP) and t-butyl phenyl phosphate (TBPP) are vapor-phase organophosphate lubricants that are highly effective in preventing wear and oxidation in high-temperature macroscopic applications [4–7]. They were suggested for MEMS applications as early as 1998 [8]. But organophosphates are not known to form chemical bonds with OTS or silicon and as such are only physically adsorbed.

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Therefore, whether they could adsorb onto OTS and/or silicon substrates in significant enough quantities to effectively protect and lubricate has remained an outstanding question. Thus motivated, we have employed a quartz crystal microbalance (QCM) to measure the uptake and nanotribology of TCP and TBPP layers adsorbed from the vapor phase onto amorphous silicon, polycrystalline silicon and octadecyltrichlorosilane (OTS) treated silicon substrates. About 3–5 monolayer-thick organophosphate films are observed to form readily on all three substrates. The coatings moreover are observed to exhibit interfacial slippage and/or viscoelasticity in response to the oscillatory motion of the QCM, implying that both enhanced protection and tribological performance may be expected for MEMS applications.

Friction Measurements by Means of QCM

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 [9]. The QCM technique is particularly well adapted for measurements of uptake rates of vapor-phase lubricants, providing a sensitive, real-time means for monitoring mass uptake [10], and tribological properties of the adsorbed film and/or its reaction products [7, 8, 11]. 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 [12].

Quartz crystal microbalance are classified according to the way the wafer is cut relative to the natural crystallographic orientation of quartz. Polished grade, 5 MHz, AT-cut (transverse shear mode) crystals were employed for these studies¹. Metal film electrodes evaporated onto the two major faces of the crystal serve as the substrate for adsorption studies.

Uptake of lubricant films from the vapor phase onto the metal electrodes of the quartz crystal produces a change in the resonant frequency that is proportional to the fraction of the mass of the condensed film that tracks the oscillatory motion of the underlying substrate. Sensitivities of tenths to hundredths of a monolayer are typical [9]. Adsorption can also produce amplitude shifts due to frictional shear forces exerted on the surface electrode by the adsorbed film. These may arise from interfacial slippage of the layer, or alternatively visco-elastic effects within the film. For the case of interfacial slippage, characteristic slip times τ , and

friction coefficients (e.g., shear stresses per unit velocity) η , are determined via [13, 14]:

$$\eta = \frac{\rho_2}{\tau} \delta(Q^{-1}) = -4\pi\tau\delta f_0 \quad (1)$$

where ρ_2 is the mass per unit area of the adsorbed film. $\delta(Q^{-1})$ is the change in inverse quality factor and δf_0 is the change in frequency of the QCM quartz crystal. The slip time is inversely proportional to friction and corresponds to the average time for the film's speed to fall to 1/e of its original value, assuming that it was pushed at a constant speed and then released, allowing frictional forces to bring it to a stop. Longer slip time indicates lower friction between the film and the substrate.

After sample electrodes were prepared (as described in detail in the next section), they were fitted into a pair of metal spring clips, which were mounted onto the electrical connections of a vacuum feedthrough, to provide mechanical support and electrical contact to external Pierce oscillator circuitry. The vacuum feedthrough was attached to an oil-free vacuum system that was subsequently pumped to a base pressure of 10^{-1} Torr.

Once the system reached this base pressure and the oscillator frequency had stabilized, the valve to the ion pump was closed and the uptake measurements were performed. Samples were exposed to TCP [15] or commercial grade TBPP [16], which was contained within a crucible held in a tungsten loop within the vacuum chamber. The crucible was located right below the experimental crystal and outgassed in vacuum before exposure to the sample. Current to the crucible was gradually increased to approximately 5 Amp, the point at which vapor uptake on the QCM became detectable. The temperature of the crucible at this point was less than 100 °C. Data for pressure, frequency, and vibrational amplitude were then recorded for a period of approximately 1 h. Quality factor shifts were obtained from the amplitude data through calibration with nitrogen gas adsorption after completion of the uptake measurements [14]. Deposited masses and slip times were then calculated for each system.

Tricresylphosphate and t-butyl phenyl phosphate uptake measurements were performed on three categories of substrates: (1) "Amorphous silicon," for data recorded on silicon films received directly from Maxtek Inc. [17] and cleaned according to the procedure described below, (2) "Polycrystalline silicon," for data recorded on polycrystalline silicon films that were deposited by solid source Si-Ge molecular beam epitaxy (MBE) and cleaned according to the procedure described below, and (3) "OTS/Si," for data recorded on OTS-coated silicon films that were prepared according to the procedure described briefly below and in more detail in Ref. [18]. Details on the sample preparation and characterization are presented next.

¹ AT-cut quartz crystals, which are oriented 35°15' from the primary crystalline axis, are readily available because the resonant frequency for crystals oriented at this angle are highly insensitive to temperature changes when operated at room temperature.

Sample Preparation and Characterization

Amorphous Silicon and OTS/amorphous Silicon

The amorphous silicon samples on commercial quartz crystals were obtained from Maxtek Inc. [17] with thin layers of silicon and Au/Cr metal pre-deposited onto both sides. They consisted of 100 nm of 99.999% pure Si deposited atop 290 nm of 99.999% of pure Au deposited atop 400 Å of Cr.

The samples were cleaned employing a slightly modified procedure from that employed previously by Brzoska et al. [19]. The cleaning process involved six steps: (1) thoroughly washing the samples with running water, (2) a rinse with DI water, (3) immersion in 0.05 M NaOH solution for approximately 30 min, (4) UV/O₃ treatment for 30 min, (5) immersion in ethanol for approximately 30 minutes, and (6) a second UV/O₃ treatment. The second UV/O₃ treatment was included to remove remaining traces of contaminants. The UV/O₃ process results in a thin (~1 nm) oxide on the surface [20].

After cleaning, the silicon samples were either mounted directly within a vacuum chamber for TCP or TBPP uptake measurements, or alternately immersed in a solution of hexadecane and chloroform (4: 1 by volume), in preparation for OTS uptake.

The solution temperature was regulated to 20 ± 0.05 °C. OTS was then injected into the solution and allowed to assemble on the samples. After removal from the liquid, the samples were rinsed to remove excess OTS so leave in place a monolayer. Complete details are reported in Ref. [18].

Polycrystalline Silicon

For the case of polycrystalline samples, Cu electrodes ~100 nm thick were deposited on both sides of the QCM. The approach required substantial development efforts to prepare polycrystalline samples in efforts to simulate silicon that is more likely to be present in actual MEMS devices. The process minimizes interdiffusion with the copper and is completed at temperatures that maintain the oscillation properties of the crystal. A schematic of the QCM structure is shown in Fig. 1. A layer of Ti ~100 nm thick was deposited by UHV e-beam metallization at room temperature on both sides, and acted as a buffer layer to prevent the alloying of the Cu electrode and the 100 nm thick Si_{0.6}Ge_{0.4} layer, which was grown at 400 °C in UHV conditions. The Si-Ge layer was introduced to provide a crystalline template prior to the deposition of the 100 nm Si layer, which was also grown at 400 °C. The Si_{0.6}Ge_{0.4} and Si layers were grown in a solid source Si-Ge molecular beam epitaxy (MBE) system. A similar sample structure

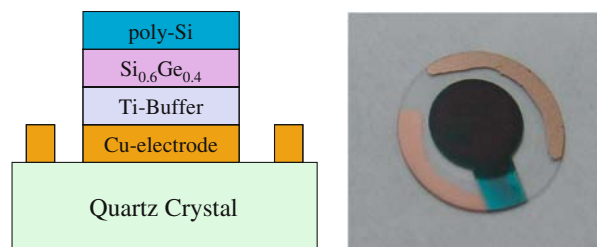


Fig. 1 A side view schematic of the multilayer structure (not to scale; see text for actual dimensions) on a QCM substrate, and an actual photograph of the QCM (3/8 inch diameter) after deposition of all layers

was employed to prepare a QCM with a-Si on the surface. These structures omitted the SiGe layer.

A typical XPS spectrum is shown in Fig. 2. The measurements indicate that the as prepared sample surfaces are free of O and C contamination. Moreover, the scans do not show the presence of Cu or Ge which indicates that the surface is Si and that alloying or diffusion of Cu or Si-Ge did not affect the Si surface layer.

Raman spectroscopy measurements of QCM samples grown at 400 °C are shown in Fig. 3. The spectra were obtained in a backscattering geometry using 514.5 nm radiation from an Ar ion laser. Raman spectroscopy provides information about local bonding and domain order. Narrow Raman peaks indicate a more ordered grain structure while broad peaks are associated with amorphous film structures.

Figure 3a shows an amorphous Si (a-Si) peak at ~ 480 cm⁻¹, while Fig. 3b shows peaks indicative of Si-Ge and Ge-Ge bonding, as well as peaks of Si in a Ge environment and the crystalline Si (c-Si) peak at ~ 520 cm⁻¹.

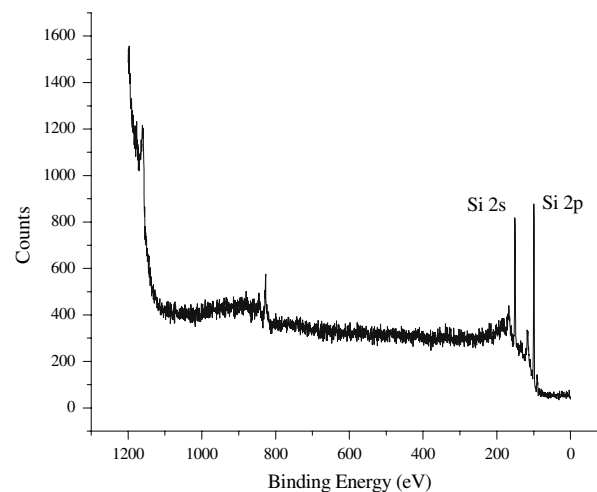


Fig. 2 XPS spectra of Si/Si_{0.6}Ge_{0.4}/Ti/Cu QCM sample, showing an absence of O and C contamination and Si 2s and 2p peaks. The spectra also indicate that Cu-Si-Ge alloying is non-existent

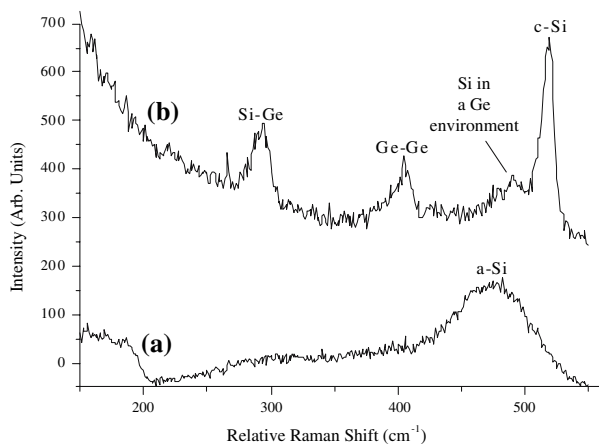


Fig. 3 Raman spectroscopy of QCM samples grown at 400 °C, using 514.5 nm radiation. The spectrum shown in (a) represents a structure without the SiGe layer, while spectrum (b) is from a sample that includes the SiGe layer. The presence of a-Si is confirmed by peak features located at $\sim 480\text{ cm}^{-1}$, as shown in (a). Features of c-Si are confirmed by the peak at $\sim 520\text{ cm}^{-1}$, as shown in (b). The other peaks in (b) are due to the SiGe layer

These clearly demonstrate how the introduction of the additional Si-Ge layer induces crystallization of the Si film.

Atomic force microscope scans were obtained for a Si/Si_{0.6}Ge_{0.4}/Ti/Cu QCM sample and commercial quartz crystals. They are depicted in Fig. 4, with scan dimension of $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$. The scans corresponds to an rms roughness that varied between 6.31–18.42 nm. The roughness of a Si/Si_{0.6}Ge_{0.4}/Ti/Cu QCM surface also depends on the growth temperature. The higher the temperature, the rougher the surface.

Results

Adsorption of TCP and TBPP of Amorphous Silicon

Figure 5 presents characteristic data sets for deposited mass and inverse quality factor shift data for vapor-phase lubricant (TBPP and TCP) adsorption on amorphous silicon surfaces at room temperature for 1 h exposure periods. The frequency shift corresponding to one monolayer of TCP is about 10.6 Hz. Although TBPP is not a pure material, a ‘monolayer’ of its constituents would result in a frequency shift on the same order as TCP. The uptake of both TCP and TBPP are similar, but we observe more slippage in the case of TCP, as indicated by greater shifts in the inverse quality factor in combination with Eq. (1)

The slip time can be derived from Eq. (1) using the change in the inverse quality factor and frequency shift, which are obtained experimentally. Slip time (τ) can then be calculated for each system using equation shown below.

$$\tau = \frac{\delta\left(\frac{1}{Q}\right)}{4\pi\delta f_0} \quad (2)$$

The data reveal that TCP slides readily on this silicon surface, characterized by slip times on the order of 0.9 ns. The slip time of TBPP on the same silicon surface is shorter (0.3 ns). The results are summarized in Table 1.

Adsorption of TCP and TBPP on Polysilicon

Figure 6 presents characteristic data sets for deposited mass and inverse quality factor shift data for vapor-phase lubricant (TBPP and TCP) adsorption on polycrystalline silicon at room temperature for 1 h exposure periods. TCP uptake on the surface is substantial, with the equivalent of five monolayers of material adsorbing in 1 h. TBPP uptake is slightly lower, with three layers of material adsorbing after 1 h.

The inverse quality factor data reveal that TBPP slides on the polycrystalline surface, characterized by slip times on the order of 0.25 ns. The slip time for TCP is shorter (0.14 ns). The results are summarized in Table 1.

Adsorption of TCP and TBPP on OTS-coated Silicon

Figure 7 presents characteristic data sets for deposited mass and inverse quality factor shift data for vapor-phase lubricant (TBPP and TCP) adsorption on ozone-cleaned and OTS-coated polycrystalline silicon at room temperature. Both TCP and TBPP uptakes are very similar with slightly smaller slippage in the case of TBPP.

The inverse quality factor data reveal that TCP readily slides on the OTS-coated silicon surface, characterized by slip times on the order of 0.48 ns. The slip time for TBPP is slightly shorter (0.24 ns). The results are summarized in Table 1.

Discussion

Abdelmaksoud et al. recently published QCM measurements of the nanodynamical properties of TCP reaction films forming on metal and oxide substrates [7, 8]. Their results marked the first nanodynamical characterization of films with known macrotribological properties, and opened a vital new pathway for studies connecting the nanoscale with the macroscale [7]. Figure 8 presents a subset of the data sets presented in Ref. [7], demonstrating the central results of that work. TCP reaction films that fail as macroscopic lubricants exhibit no slippage at the atomic scale, evidenced by a lack of change in the inverse quality factor during gas uptake (open circles). Successful (macroscopic)

Fig. 4 The morphology of Si-film on QCM measured by AFM at different growth temperatures

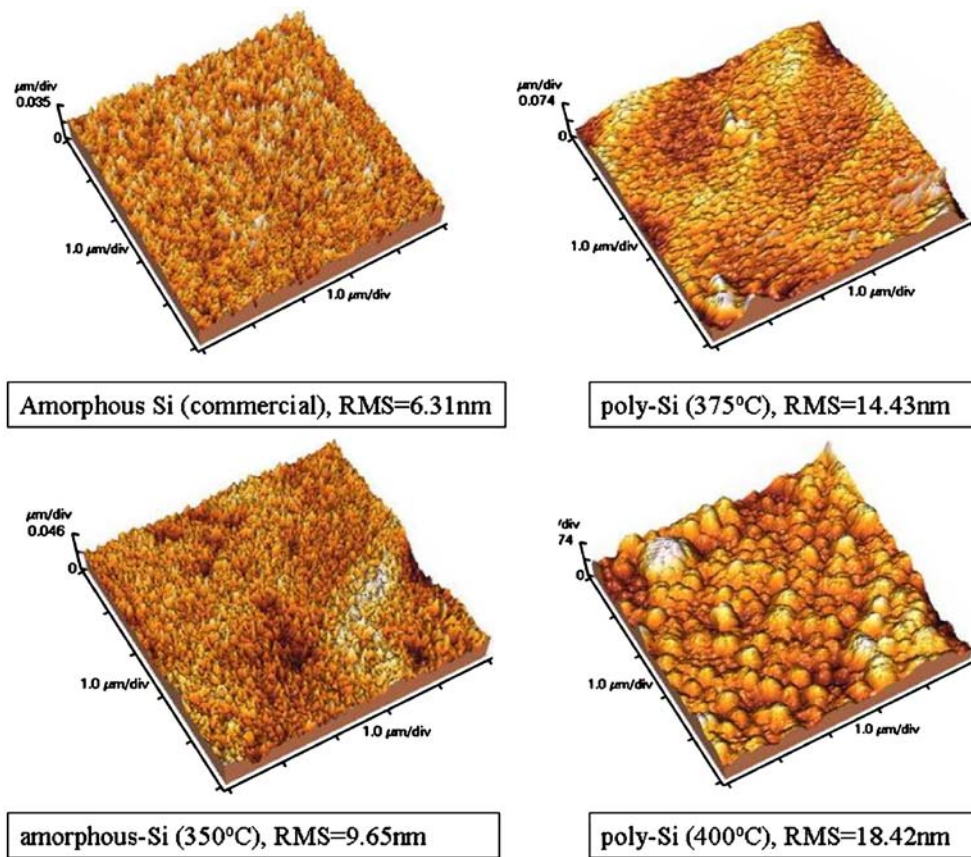
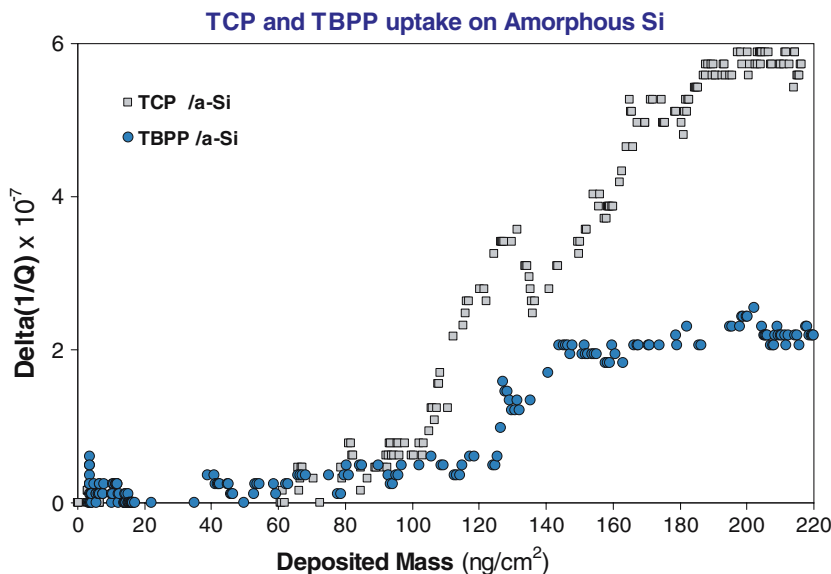


Fig. 5 Deposited mass and Q^{-1} shift data for TCP uptake on amorphous silicon (filled squares) and TBPP uptake on amorphous silicon (filled circles)

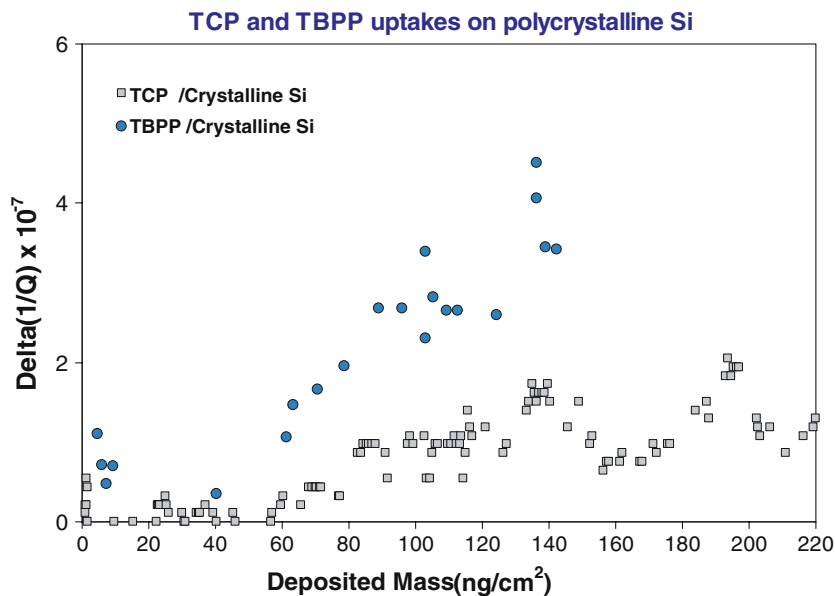
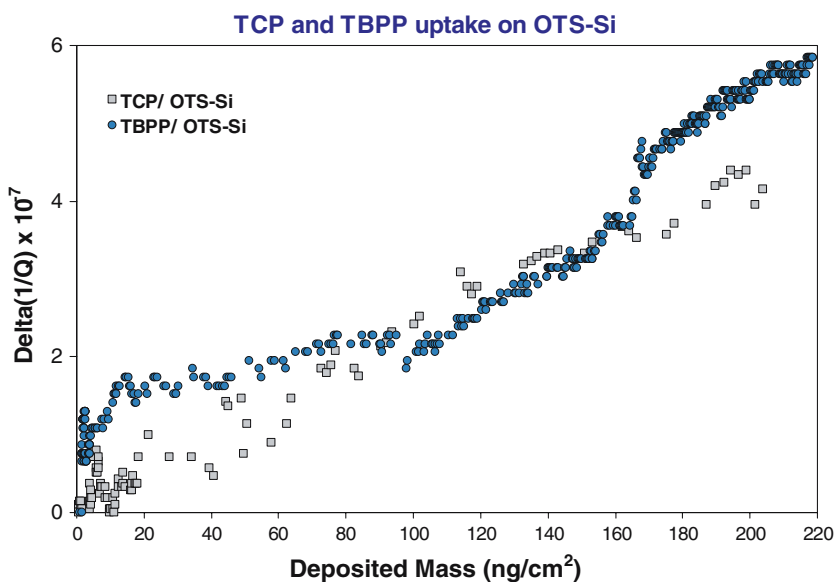


lubricants meanwhile exhibit non-zero shifts in inverse quality factor (open squares and closed circles) and trace levels of slippage as detected by the QCM. Careful analysis of the data ruled out substantial contributions from viscoelastic effects within the films, firmly supporting the notion that slippage is highly beneficial so long as the material remains attached to the substrate.

Within the present context, it is desirable the organophosphate exhibit beneficial tribological properties on both OTS and silicon, as the MEMS application will require lubrication of both the OTS and worn surfaces. Since all organophosphate and organophosphate + OTS combinations studied have non-zero slip times, the materials are potential candidates for silicon MEMS systems. We

Table 1 Summary of experimental results from TBPP and TCP uptake on polycrystalline silicon, amorphous silicon and OTS surfaces. The film thickness is listed in units of “monolayers”

Vapor Phase Lubricant	Polycrystalline silicon		Ozone-cleaned amorphous silicon		Si+OTS	
	Film thickness (monolayer)	Slip time τ (ns)	Film thickness (monolayer)	Slip time τ (ns)	Film thickness (monolayer)	Slip time τ (ns)
TCP	5	0.14	5	0.90	5	0.48
TBPP	3	0.25	5	0.30	5	0.24

Fig. 6 Deposited mass and Q^{-1} shift data for TCP uptake on polycrystalline silicon (filled squares) and TBPP uptake on polycrystalline silicon (filled circles)**Fig. 7** Deposited mass and Q^{-1} shift data for TCP uptake on OTS-coated silicon surface (filled squares) and TBPP uptake on OTS-coated silicon surface (filled circles)

attribute the variability of the nanodynamical properties associated with the various silicon surfaces to the surface morphology of the silicon. The combination of an organophosphate + OTS appears most likely to provide more consistent tribological properties. TBPP appears to be the

preferable candidate from several points of view, including the reduced toxicity of the material itself with respect to TCP. TBPP moreover exhibits non-zero levels of slippage with relatively large levels of adsorbate coverage. Given that TBPP is an excellent high-temperature as well as an

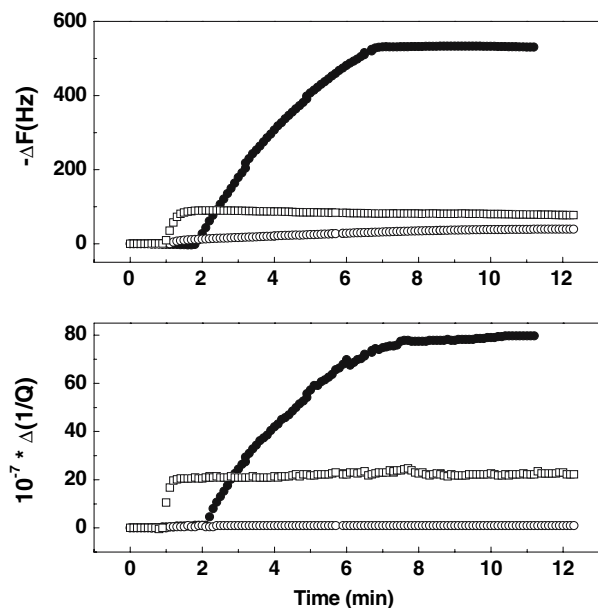


Fig. 8 Frequency and Q^{-1} shift data for systems that are lubricious (filled circles: oxygen/TCP/Fe and open squares: TCP/oxygen/Fe) and are not lubricious (open circles: oxygen/TCP/Cr) at the macroscopic scale. (See ref. 7)

anti-oxidant, it shows great promise for protecting OTS layers from environmental degradation at elevated temperatures. Synergism of lubricant combinations has in fact been observed in the past for certain other lubricant combinations [21]. Future studies will investigate this possibility for organophosphate + OTS combinations on actual silicon MEMS devices.

Conclusions

Adsorption measurements of tricresylphosphate (TCP) and t-butyl phenyl phosphate (TBPP) layers adsorbed from the vapor phase onto silicon, and octadecyltrichlorosilane (OTS) treated silicon surfaces have been performed with a quartz crystal microbalance, yielding values for total adsorbed monolayers and molecular slippage. The values are summarized in Table 1.

Uptake on Silicon Substrates (Amorphous and Polycrystalline Silicon)

Tricresyl phosphate and t-butyl phenyl phosphate both adsorb readily on silicon substrates, with TCP and TBPP film thicknesses of five layers in 1 h being possible. Since the coatings are observed to exhibit interfacial slippage and/or viscoelasticity in response to the oscillatory motion of the QCM, both enhanced protection and tribological performance may be expected for MEMS applications. It is

unknown whether a slightly increased slip time will impact the performance of the material. The structure of the silicon itself, (i.e., amorphous or polycrystalline) did not appear to impact whether or not the lubricant slips, which is the most significant indicator of tribological performance according to Ref. [7].

Uptake on OTS Substrates

Both TCP and TBPP slide readily on OTS coated-silicon surfaces. TCP and TBPP were able to form 5–6 monolayers in the same time period. Both TCP and TBPP exhibit interfacial slippage, with the TCP being twice more mobile. Since the coatings are observed to exhibit interfacial slippage and/or viscoelasticity in response to the oscillatory motion of the QCM, both enhanced protection and tribological performance may be expected for MEMS applications compared to OTS alone.

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