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General aspects of solid on liquid growth mechanisms

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Abstract: Liquids, in general, tend to have a lower density as solids and therefore it is not straightforward to deposit solid over liquids in a way that the liquid becomes hermetically sealed under the solid layer. The authors review that several phenomena that can easily be observed in nature are only due to particular anomalies and solid on liquid is rather an exception as the rule. Natural solid on liquid systems are lacking of thermal, mechanical or chemical stability. It is not surprising, that one is not at all used thinking about to e.g. replace the gate oxide in a thin film transistor by a thin film of oil, or, to find in other microsystems functional liquids between a stack of thin solid films. However, once this becomes a serious option, a large variety of new Microsystems with new functionalities can be easily designed. In another paper (this conference and [1]) the authors pioneered that the polymer Parylene (poly(p-xylylene)) can be deposited on liquids coming already quite close to the above mentioned vision. In this paper the authors ask if one can synthesize other solid on liquid systems and surprisingly conclude, based on experimental evidence, that solid on liquid deposition seems to rather be the rule and not the exception.

1. Introduction

Daily observation seem to exclude coverage of solid layers on liquids due to the principle of Archimedes, that is based on density considerations. Exceptions are due to special designs of mechanically pre-formed cans or ships allowing to bottle liquids into solid containers and gravitation is not anymore the selection criterion for what will be above or below and what is substrate or coating. The most striking solid on liquid system that can be observed in nature is certainly based on the anomaly of water-density that is highest at 4°C. By that ice coverage of lakes as soon as phase transition from liquid to solid occurs. As another case stressing anomalies is the fact that mercury as a liquid has a particular high density and the successful experiment shown in figure 1 seems to be straightforward. In this experiment paint sprey was applied over mercury droplets.

The analysis of the growth mechanism can be given as follow: the paint covers the surface of mercury and will, due to density consideration not sink to the bottom of the droplet. It could happen that the mercury first prevents polymerization at the interface, however the high rate application of paint let dominate its concentration and after an interfacial layer the pure paint will polymerize resulting to a first synthetic solid on liquid system.

Looking at low-density liquids it is no longer possible to count on a Mercury effect. Let us assume that precursors from a vapor or liquid phase arrive on the surface of the liquid. If a solid layer should be synthesized, two basic mechanisms could predict successful solid on liquid deposition: First, the
precursors remain on the surface and cross-link in order to form a layer. In this case the liquid substrate behaves like a solid substrate.

![Figure 1. a, b Paint spray on mercury after polymerization.](image)

In this case linear growth of the solid layer is predictable. Second, the polymerization is induced by a precursor and the interaction between the molecules of the liquid substrate. In this case the growth is in the beginning reaction limited, later diffusion limited. Hence parabolic thickness-time relationship can be predicted. For the second mechanism the oxidation of liquid aluminum can be mentioned, hereby a real solid on liquid system is existing as long as the temperature remains above 650°C.

2. Experimental
The vapor phase generation for precursor-feed can be taken from standard deposition processes for solid on solid deposition. In order to have a big choice, chemical vapor deposition (CVD) or plasma enhanced CVD (PECVD) processes are preferable. Using vacuum systems for Low-Pressure CVD or glow-discharge plasma processes, the choice of liquid substrates is strongly limited and the vapor pressure of the liquid must be well below the chamber pressure. Suitable liquids are e.g. glycerol, bis(3,5,5-trimethylhexyl) phthalate, and bis(2-ethylhexyl) adipate. In order to have more choice of liquids, CVD and PECVD have to be carried out at atmospheric pressure. In the case of CVD the creation of precursors need high temperatures that let, again, evaporate the liquid substrat. In the case of atmospheric PECVD, a cold corona was applied in a so-called silent discharge configuration as proposed by [2].

Using liquid precursors to create solid on liquid systems is similar from the two layer-forming mechanisms described above. The following experimental conditions must be at hand:
1. Two non-miscible liquids.
2. Casting a lower density top liquid onto a higher-density bottom liquid.
3. The top liquid undergoes a phase transition either by itself or by a chemical reaction induced from the bottom liquid.

3. Results and discussion
Putting a glycerol droplet on the bottom electrode of a RF (13.56 MHz) driven parallel plate reactor using the radical of plasma-induced dissociation of ethylene gas at 50 Pa pressure, led immediately appear a solid amorphous carbon layer that covers the droplet. As shown in figure 2a, strong internal tensions let appear pronounced wrinkles: the liquid in its role as substrate is unable to compensate the stress induced from nucleation and subsequent polymerization of the solid layer.

In a second experiment of the same category, just by replacing ethylene gas by HMDSO (hexamethyldisiloxane) vapour, again at 50 Pa pressure, a similar phenomenon can be observed; in this case a layer similar to quartz is grown on the liquid. Again strong wrinkles indicate the internal tensions of the layer. The results are shown in figure 2b.
Figure 2. a) PECVD of a polymer carbon layer from an ethylene glow-discharge on a glycerol droplet; b) PECVD of Si$_x$O$_y$ from a HMDS-O glow-discharge on glycerol; c) atmospheric pressure PECVD of a fluor-polymer layer on glycerol from a Ar/CF$_4$ mixture corona discharge.

Going to atmospheric pressure PECVD, CF$_4$ is used as gas to be dissociated by the corona discharge. Again, a thin layer is grown and identified as fluorine-polymer layer. It contains apparently less internal stress as the better replication of the solid layer on the liquid shows in figure 2c.

In order to find representative systems that rely on the second growth mechanism, liquid PDSM (polydimethylsiloxane) without curing agent is used as liquid substrate. Running an Ar / H$_2$ plasma at 50 Pa pressure, let atomic hydrogen induce polymerization of PDMS occurs in the vicinity of the surface because lack of curing agent in the liquid. Here a solid PDMS layer is grown as shown in figure 3. We show by deposition-time thickness measurements that the reaction in the beginning proceeds faster (reaction limited) and becomes diffusion-limited because the growing layer reduces the atomic hydrogen supply to the reaction zone.

![Figure 3](image3.jpg)

**Figure 3.** Surface polymerization of liquid PDMS due to atomic hydrogen exposure from a Ar/H$_2$ glow discharge plasma at 50 Pa and 13.56 MHz plasma excitation frequency. The wrinkles at the surface indicate the stress that is exerted due to polymerization.

![Figure 4](image4.jpg)

**Figure 4.** After evaporation of the solvent a stable THV 220 layer is formed over liquid of fluorescin.

![Figure 5](image5.jpg)

**Figure 5.** Solid on liquid system based on sol-gel solidification of the top liquid.
In the next experiments were carried out using liquid precursors. As a first approach the fluorinated polymer called THV 220 [3] is completely dissolved in e.g. ketone. THV 220 dissolved in MEK (methyl ethyl ketone) is casted on higher density liquids. Evaporation of the solvent let cross-link the macromolecules and replicate the macroscopic shape where the liquid was cast on, shown in figure 4. Here, a kind of bridge-building effect can be observed, starting from the outer border.

A further approach using liquid precursors is demonstrated using TEOS on an ionic liquid. The sol-gel reaction in the top liquid forms SiO$_2$ creating by that a solid layer that covers the bottom liquid as shown in figure 5.

4. Conclusions and outlook
It is foreseen that stable solid on liquid deposition (SOLID) systems have the potential to further expand the technological possibilities looking at architecture and design of next generation Microsystems. In such systems the liquid can just be passive as Volume-placeholder being subsequently removed as sacrificial liquid for caverns and channels creation, as needed in the field of fluidic systems. For other applications the liquid will be active, containing molecules or particles that remain functional in the liquid or that functionalize the overgrowing solid by chemical reaction. Based on simple models, the authors predicted growth mechanisms that have been experimentally brought to evidence in this paper. It can be assumed that e.g. the precursors coming from the gas phase will not necessarily disappear from the surface by sinking below the liquid surface since inter-molecular forces at the surface are much more important than gravitational effects. As soon as precursors accumulate at the surface and cross-link, linear polymer growth is observed. The authors could bring to evidence such a behavior for all tested CVD and PECVD examples that have been successfully tested without any exception. If the precursors react with the liquid, transition from reaction-limited to diffusion limited growth is observed.

In summary, our preliminary study let us conclude that solid on liquid deposition is rather the rule than the exception.

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