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Ultra-Transparent Atomic Layer Deposition Membranes for Liquid Cell TEM

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Liquid cell electron microscopy (LCEM) has enabled the direct *in-situ* visualization of a range of physical and chemical processes at high spatial resolution. Various designs of liquid encapsulating cells have enabled LCEM, including "sandwiches" of two membrane chips glued to one another, monolithic microfluidic channels, and flow cells which use an O-ring to seal the liquid [1]. However, these approaches typically make use of silicon nitride (SiN) membranes, which are robust under electron radiation, chemically inert, and compatible with conventional silicon micro-fabrication techniques, making the production of these cells scalable. However, these cells suffer from significant drawbacks, including the low conductivity of SiN, and the high scattering cross section of typical membranes, which limits achievable resolution in the microscope. On the other end of the spectrum, researchers have made use of graphene liquid cells [2], which leverage the high conductivity and ultra-low scattering cross-section of graphene. However, these cells involve manual transfers of graphene on TEM grids and cannot be produced in a scalable fashion.

To overcome such challenges, we have fabricated liquid cells using atomic layer deposition (ALD) films, which are engineered to provide properties desirable in a good encapsulating cell for LCEM, namely, low thickness, high electronic conductivity, high crack resistance, and most importantly, a scalable microfabrication process. We use a ~ 20-50 nm thick stacks of alternating layers of TiN/SiO_x as the encapsulating membrane. Being a conducting ceramic, the TiN layers offer high charge densities (~10^{21} cm^{-3}), improving electrical conductivity of the films and minimizing charging effects, while SiO_x layers prevent crystalline grain growth in the TiN, add crack resistance, and allow us to functionalize the surface for increased hydrophilicity. The successful fabrication of these cells (shown in Figure 1(a)) relies on the use of a novel polymeric sacrificial layer, which also serves as a suitable substrate for ALD[3].

To study the efficacy of these ALD films as viable membranes for LCEM, we used e-beam induced reduction of an aqueous solution of chloroauric acid ($HAuCl_4$). This is a well characterized liquid cell TEM experiment [4] in which the incident e-beam reduces the dissolved Au^+ ions to Au^0 atoms and initiates the growth of Au nanoparticles. We find that we are able to reproduce results from previous studies, as evidenced in Figure 2, showing that these ALD films serve as robust encapsulations, while providing the aforementioned advantages. Due to relatively high electron transparency of the encapsulating films, we are also able to successfully image the resulting Au crystals at atomic resolution in a liquid phase.

This approach can also be easily extended to other material systems one can deposit via ALD, opening possibilities for adding further functionalities to these liquid cells. Moreover, the lower limits of the thicknesses of ALD membranes are yet to be explored, and further improvements in electron transparency of the liquid cells can possibly yet be made to enable studies of low contrast systems in the liquid phase [5].

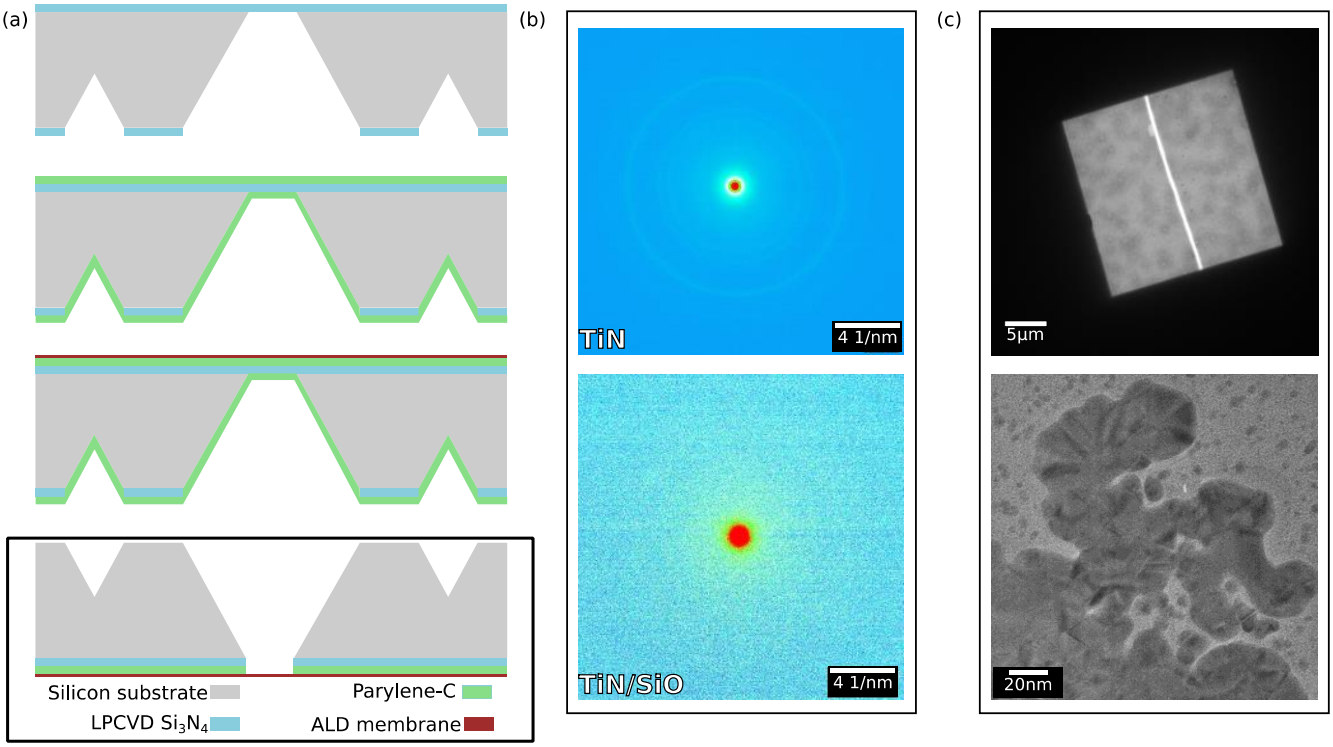

Figure 1. (a) Shows the nano-fabrication process for obtaining suspended, ultra-thin ALD membranes. Electron diffraction shows that a ~50nm thick layer of ALD TiN is nano-crystalline (b), but grain growth was suppressed using alternating layers of TiN/SiO_x. Liquid cells were assembled using two such membranes facing one another, and both an overview image of a liquid cell, and a high-resolution TEM image of gold nano-crystals are shown in (c).

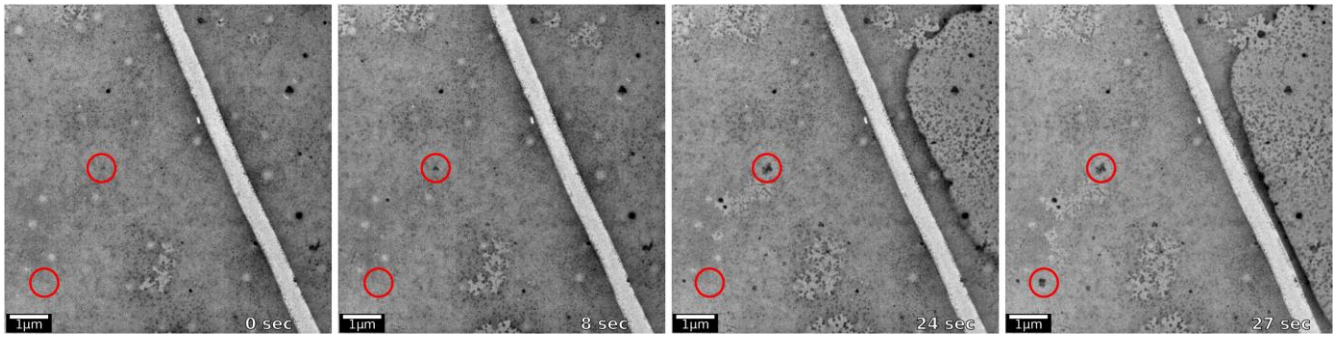

Figure 2. A sequence of frames collected under electron radiation, which leads to the precipitation of Au nano-crystals from the concentrated solution of $HAuCl_4$. Dendritic growth of crystals is observed in the "wet" regions (in red circles), indicating nucleation followed by diffusion limited growth is the likely mechanism. However, the exact growth mechanism is heavily influenced by dose conditions, and the solution concentrations.

References:

[1] FM Ross in "Liquid cell electron microscopy" (Cambridge University Press).

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[2] JM Yuk et al., Science **336**(6077) (2012), p.61.
[3] MJ Elowson et al., Journal of Vacuum Science & Technology B **40**(2) (2022), p.023001.
[4] Y Zhang et al., Chemistry of Materials **29**(24) (2017), p.10518.
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