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Open-hardware, High-vacuum Storage for TEM Holders Remedies and Quantifies Hydrocarbon Contamination

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Hydrocarbon contamination plagues high-resolution electron microscopy by depositing carbonaceous layers onto surfaces during electron irradiation, which can render carefully prepared specimens useless [1-4]. Hydrocarbon deposition causes beam broadening with increasing specimen thickness [5] that degrades resolution alongside loss of contrast [6]. Due to the large inelastic cross-section of carbon, even small quantities can hamper accurate atomic species detection in electron energy loss spectroscopy (EELS) [7]. Oxygen and water molecules pose problems of lattice damage by chemically etching the specimen during imaging [8]. These constraints on high-resolution and spectroscopic chemical imaging demand clean, high-vacuum microscopes with dry pumps. However, even the cleanest microscope columns suffer from impurities desorbed off specimen holders or the specimen itself [9]; especially problematic in experiments imparting large dose as energized electrons exacerbates organics polymerization onto specimen [10, 11].

Here, we present an open-hardware design of a high-vacuum manifold (Fig. 2) that stores multiple transmission electron microscope (TEM) holders to remedy hydrocarbon and residual species exposure. To confirm the effectiveness of high-vacuum storage, we quantify the molecular species adsorbed onto TEM holder surfaces under various storage conditions using a residual gas analyzer (RGA) as part of our design. Partial pressure measurements from RGA detect and infer chemical species by their mass-charge ratio. Users can directly assess the the composition and cleanliness of holders or specimens. Initial RGA measurements across 7 different TEM holders demonstrate most are inherently dirty and overnight storage in a desiccator cabinet will introduce a range of unwanted chemical species into vacuum.

The RGA spectrum for a typical TEM holder (Fig. 1) highlights the range of species spanning organics of various carbon compositions, viscous pump oil, water and oxygen, that totals a manifold pressure of 10^{-4} – 10^{-5} Torr (hPa). These contaminants originate from atmospheric organics, microscope pump oil and o-ring vacuum greases – all of which can accumulate on TEM holder surfaces without proper storage and regulation. A typical TEM column requires evacuation down to 10^{-7} Torr (hPa). by turbomolecular (dry) or diffusion (oil) pumps operating in the high vacuum (HV) range [12]. When a TEM holder is clean, the manifold can achieve total pressure as low as $\sim 7.5\times10^{-8}$ Torr (10^{-7} hPa), which is the usual limit of o-ring sealed systems. Adsorption coverage described by Langmuir (sticking coefficient = 1) will form one monolayer per second at pressures of 10^{-6} Torr [13]. Reducing partial pressures of contaminants below 10^{-10} Torr (the RGA detection limit) prevents monolayer adsorption during a typical TEM experiment.

Our high-vacuum manifold effectively reduces contaminant partial pressures by ~4 orders of magnitude to below 10^{-10} Torr, using overnight storage and bakeout inside manifold. With overnight high-vacuum storage alone, residual gas levels across the whole spectrum reduce by 1–2 orders of magnitude ($\sim 10^{-7}$ Torr) and promotes shorter vacuum recovery time (Figure 1). A TEM holder exposed to ambient air for 10 minutes (roughly the time to load a specimen) after high-vacuum storage achieves partial pressure recovery 2–4 times faster than that of a holder stored in ambient air. This suggests that users can achieve faster pressure recovery within the TEM column and have more efficient microscopy sessions with high-vacuum storage.

The additional bakeout system is exceptional at removing problematic pump oils and reducing atmospheric species (i.e. CO, H_2O, etc.) by an additional 2 – 3 orders of magnitude down from high-vacuum storage and ~4 orders lower compared to storage in ambient air (Fig. 1). Bakeout of TEM holders, and specimens held therein, is carried out inside the manifold at 130 ºC for 48 hours as organic molecules desorb at this temperature [14,15] without degrading o-rings (Viton ~225ºC, Buna ~120ºC) and internal wiring components of a TEM holder. By facilitating organic desorption, pump oil and most of the heavier species above 35 amu were below the RGA's detectable limit (partial pressure < 10^{-10} Torr). Bakeout at temperatures (150-250 ºC) above the binding energies of gas molecules (0.73-1.08 eV/molecule) minimizes migration driven by surface diffusion of organic molecules that do not immediately desorb in vacuum [16,17]. With that, the manifold achieves its lowest total pressure of ~7.5×10^{-8} Torr (10^{-7} hPa) even when a holder is stored. We determine that thermal bakeout in vacuum exhibits higher performance over chemical cleaning which leaves organic residue [18] and plasma cleaning that may damage carbon-containing specimens and only removes thin layers of surface hydrocarbons [19].

Our design consists of a 2-tier structure can store up to 10 TEM holders (Fig. 2d). Each holder port is fabricated to fit JEOL and FEI holders and can be closed with butterfly valves when holders are in-use. The number of tiers and ports can be easily customized to suit a facility's needs. The bakeout system consists of a quartz lamp on electrical feedthrough installed in the mini side port of storage flanges (Fig. 2b, top left). This allows for radiative heating of TEM holder tip and specimen (if mounted) up to ~150 ºC while in vacuum. Bakeout temperature is variable with applied electrical potential. Operation of manifold requires only a few minutes of training.

Open-source blue prints, part lists, and costs are provided for all electron microscope facilities [20].

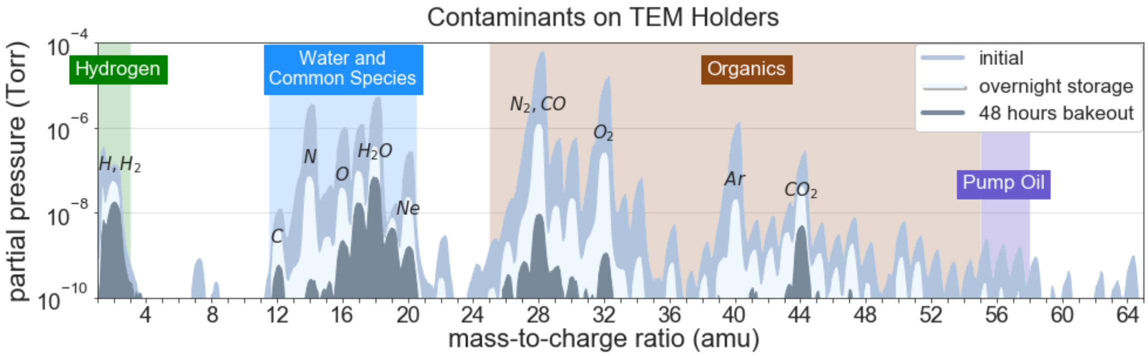

Figure 1. RGA spectrum of a dirty JEOL TEM holder from overnight high-vacuum storage and bakeout at 130ºC for 48 hours. Shaded regions highlight chemical species which commonly degrade electron micrographs. Specifically, oxygen and water (16–18 amu), organics molecules (25–55 amu) and pump oil hydrocarbons (55–59 amu) are typical regions of concern for microscopists. High-vacuum storage lowers residual gas levels accumulated from ambient conditions by 1–2 orders of magnitude. Heavier species above 35 amu including pump oil are mostly below detectable limit (<10-10 Torr).

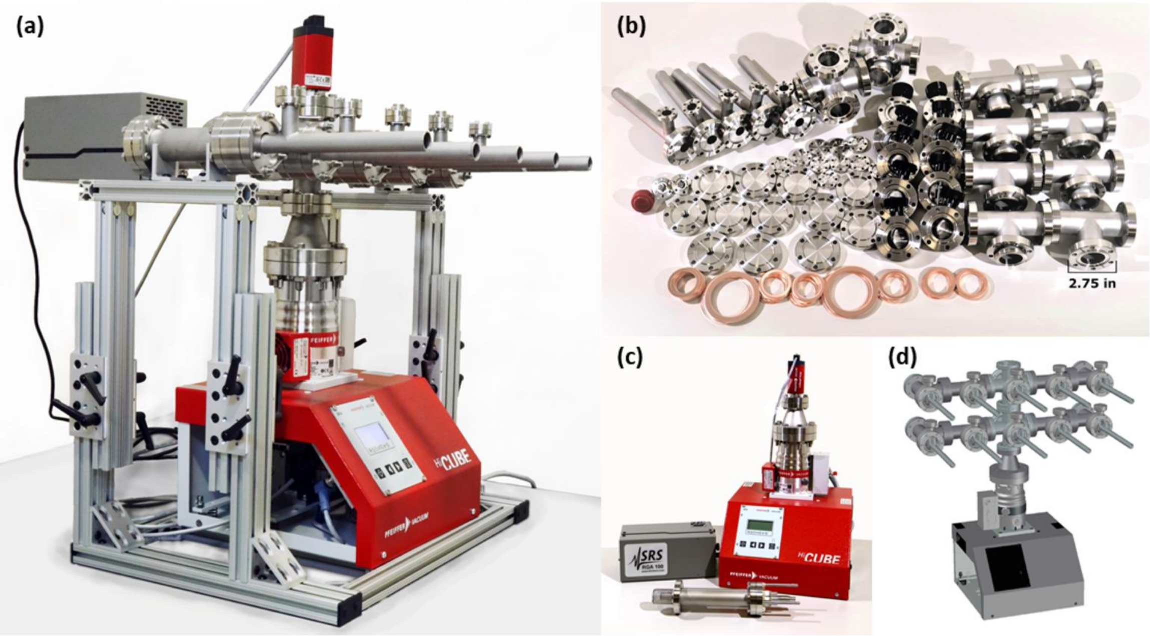

Figure 2. Components and complete set-up of vacuum manifold to store 10 TEM holders. a) Operating high-vacuum manifold on support frame at a TEM facility; our design is customizable up to 2 tiers with 10 ports. b) Vacuum compatible stainless-steel parts and copper gaskets. c) Stanford Research Systems 100 amu Residual Gas Analyzer (RGA) with quadrupole mass probe, Pfeiffer Vacuum HiCube 80 Eco turbopump station with Pfeiffer Vacuum ActiveLine PKR total pressure gauge. d) CAD drawing of manifold assembly. Design is made open-source.

References
[1] G. Love, *et al.*, Scanning **4** , 32–39 (1981).
[2] R.L. Stewart, Phys. Rev. **45**, 488–490 (1934).
[3] H.W. Conru, P.C. Laberge, J. Phys. E: Sci. Instrum. **8** (1975).
[4] J. Hillier, Journal of Applied Physics **19**, 226–230 (1948).
[5] N. de Jonge, *et al.*, Nature Review Materials **14** (2019).
[6] C. Soong, *et al.*, Microscopy Today **20**, 44–48 (2012).
[7] A.J.V. Griffiths, T. Walther, J. Phys.: Conf. Ser. **241** 012017 (2010).
[8] G.T. Leuthner, *et al.*, Ultramicroscopy **203**, 76–81 (2019).
[9] U.R. Bance, *et al.*, Vacuum. **28** (1978).
[10] H.W. Conru, P.C. Laberge, J. Phys. E: Sci. Instrum. **8** (1975).
[11] A.E. Ennos**,** Journal of Applied Physics. **4**, 101–106 (1953).
[12] D.B. Williams, C.B. Carter, Transmission Electron Microscopy: A Textbook for Materials Science, Springer-Verlag (2009).
[13] K. Jousten, Proceedings of Vacuum Technology, CERN Accelerator School (1999).
[14] K. Jousten, Vacuum **49** 359–360 (1998).
[15] R. Grinham, A. Chew, Appl. Sci. Converg. Technol. **26**, 95–109 (2017).
[16] S. Hettler, *et al.*, Micron. **96**, 38–47 (2017).
[17] B. Dayton, Trans. 8th AVS. VAC. Symp. **42** (1961).
[18] C.M. McGilvery, *et al.*, Micron. **43**, 450–455 (2012).
[19] A.J.V. Griffiths, T. Walther, J. Phys.: Conf. Ser. **241**, 012017 (2010).

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