Micron 73 (2015) 36–46

Contents lists available at ScienceDirect

Micron

journal homepage: www.elsevier.com/locate/micron

Contamination mitigation strategies for scanning transmission electron microscopy

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ARTICLE INFO

Article history:
Received 9 January 2015
Received in revised form 30 March 2015
Accepted 30 March 2015
Available online 6 April 2015

Keywords:
Scanning transmission electron microscopy
Hydrocarbon contamination
Specimen cleaning

ABSTRACT

Modern scanning transmission electron microscopy (STEM) enables imaging and microanalysis at very high magnification. In the case of aberration-corrected STEM, atomic resolution is readily achieved. However, the electron fluxes used may be up to three orders of magnitude greater than those typically employed in conventional STEM. Since specimen contamination often increases with electron flux, specimen cleanliness is a critical factor in obtaining meaningful data when carrying out high magnification STEM. A range of different specimen cleaning methods have been applied to a variety of specimen types. The contamination rate has been measured quantitatively to assess the effectiveness of cleaning. The methods studied include: baking, cooling, plasma cleaning, beam showering and UV/ozone exposure. Of the methods tested, beam showering is rapid, experimentally convenient and very effective on a wide range of specimens. Oxidative plasma cleaning is also very effective and can be applied to specimens on carbon support films, albeit with some care. For electron beam-sensitive materials, cooling may be the method of choice. In most cases, preliminary removal of the bulk of the contamination by methods such as baking or plasma cleaning, followed by beam showering, where necessary, can result in a contamination-free specimen suitable for extended atomic scale imaging and analysis.

1. Introduction

Hydrocarbon contamination has been a limiting factor in electron microscopy since the technique was invented. Vacuum systems using oil-based rotary and diffusion pumps can produce back-streaming of oil. This oil vapour can then crack under the electron beam, resulting in the build-up of carbon on the area under investigation (Ennos, 1953). Improvements in pump oils and vacuum technology in general, have greatly diminished the contribution of the vacuum system to the contamination problem. Oil-free systems, such as scroll, turbo-molecular and ion pumps have largely replaced oil-based pumps for evacuating columns (Williams and Carter, 1996). When used in conjunction with liquid nitrogen-cooled cold traps, much cleaner vacuum systems have resulted. Today, the majority of the contamination arrives on the specimen (Egerton et al., 2004; McGilvery et al., 2012; Soong et al., 2012).

Scanning transmission electron microscopy has often been limited by contamination on the specimen, especially where long mapping scans at high magnification are carried out. Strategies for dealing with contamination have been developed, and include plasma cleaning (Griffiths, 2010; Isabell et al., 1999; McGilvery et al., 2012; Zaluzec, 2001; Zaluzec et al., 1997), baking (Egerton et al., 2004; McGilvery et al., 2012; Soong et al., 2012; Williams and Carter, 1996), exposure to ultraviolet light and ozone (Hoyle et al., 2011; Soong et al., 2012), cooling (Egerton and Rossouw, 1976; Hren, 1986) and beam showering (Egerton et al., 2004). The need for such contamination mitigation strategies has been made even more pressing with the advent of aberration corrected STEM. Atomic resolution imaging and mapping is now routine, and the localised electron doses may be greater by up to three orders of magnitude than those used in conventional STEM. Often, contamination is the major limiting factor. This manifests itself as reduced lattice contrast, compromised EELS analysis (Schamm and Zanchi, 2001) and loss of resolution due to beam broadening. In general carbon deposition varies between a minor nuisance and a major obstacle.

Microscopists often develop heuristics for decontamination treatments, but these may be overly conservative and waste valuable column time. This article describes a quantitative evaluation of a range of contamination mitigation techniques, to understand not only which are best suited to particular applications but also

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http://dx.doi.org/10.1016/j.micron.2015.03.013
0968-4328/

Table 1
Specimen types, contaminants and cleaning methods used.

Sample type	Contaminant	Cleaning methods evaluated
Commercial carbon supports	Hydrocarbon – from manufacture/adding acetone	Baking, plasma, beam shower
NiO thin film on Mo grid	Silicone	Baking
Si bulk and DRAM foils	Hydrocarbon	Plasma, beam shower
PtNi nanoparticles/holey C	Oleylamine/hexane	Baking, cooling, plasma, beam shower
PbS quantum dots	TLA/methanol	Baking, plasma, beam shower

to optimise the duration of treatments required for a specific outcome.

2. Materials and methods

Various specimens were used to assess different types of contamination. These included as-received carbon films (25 nm thickness) from a commercial vendor, a commercial thin oxide reference film, cross-sections from a semiconductor device and a bulk silicon thin foil – both produced by conventional ion milling methods. Holey carbon films loaded with a nanoparticulate were prepared by dispersing the phase in organic solvent. In the case of PtNi, *n*-hexane was used, as these nanoparticles will not disperse well in polar solvents. For PbS, ethanol was used. PtNi synthesis used a long chain surfactant (oleylamine) of low volatility, while PbS involved thiolactic acid and methanol. Organic residue from synthesis was found in both phases, a commonly encountered scenario when studying chemically synthesised nanoparticulates with electron microscopy. Clean holey carbon films were also deliberately contaminated by placing a drop of acetone on them, shaking off the excess and allowing to dry. A summary of the experimental conditions evaluated is shown in Table 1.

To measure the carbon contamination rate, regions of the specimen were scanned using a standard set of STEM conditions on a JEOL ARM200F operating at 200 kV: Probe 5C, Condenser Aperture 40um, probe current 0.155 nA, scanning at 1 mx magnification (170 nm × 170 nm), for durations of 1–16 min. Scanning was done in a fast scan Preview mode: 512 × 512 pixels × 1.86 μs dwell time to produce frame rates of about 1 per second (allowing for overscan and settling time). The current density based on the nominal pixel area (0.11 nm^2) was 1.41 nA nm^2. In reality, the probe diameter (0.1 nm) was much smaller than the pixel size leading to a current density of 19.7 nA nm^2. The electron fluxes are reported in Table 2. Electron beam heating effects were calculated using the model of Egerton et al. (2004). Temperature rises were highest for low thermal conductivity carbon support films. Beam showering at 23.3 nA resulted in a 5 °C temperature rise, whereas at the measurement current (0.155 nA), the value was just 0.04 °C. In the case of Si foils, where the thermal conductivity is some 90× greater than that of carbon, the temperature rise was proportionally lower, such that beam showering resulted in just 0.05 °C of temperature change.

The cold trap was in operation and the column vacuum was 1–1.3 × 10^{-5} Pa throughout. The area for scanning was selected at low magnification (150 kx) then zoomed in to 1 mx for the duration of the irradiation. Following completion of the scan, the magnification was again reduced to 150 kx and spot mode used to mark the scanned regions with contamination dots to aid identification in energy filtered TEM (EFTEM) mode. The thickness of the carbon deposited by the scan was measured using thickness mapping (10 eV slit) on a GIF Quantum in energy filtered TEM (EFTEM) mode. The mean free path for carbon at 200 kV was calculated using the method of Iakoubovskii et al. (2008) as 150 nm. This enabled the carbon thickness to be obtained from the thickness maps.

Fig. 1a shows an EFTEM thickness map of one such scan. The outer region of interest (ROI – black square) is the scanned image size at 1 mx. The actual area scanned by the beam is larger than the scanned image area due to the over scan of the STEM. The thickness of the central segment of the scanned area (white square) was measured. This avoided thickness variations associated with the leading edge of each raster scan (Fig. 1a top left). The thickness profile measurement (white rectangle) was carried out perpendicular to the scan direction to avoid the run-on and run-off of the scan, which caused contamination build-up outside the main scan area. The thickness profile (Fig. 1b) was used to measure the step function in thickness compared with the contamination-free environs of the scanned area. The thickness of the film either side of the scanned area was measured and averaged. This was subtracted from the thickness in the centre of the scanned area to yield the contamination thickness. This eliminated the effect of any minor global build-up of contamination during set up at 150 kx.

Baking was carried out using a JEOL JEC-4000DS dry pumping station. This turbo-pumped system had a quartz heater below the holder and raised the temperature to about 110 °C. There was no vacuum gauge on the system, but the pressure was probably in the 10^{-3} Pa range. The plasma cleaner was a JEOL EC-52000IC Ion Cleaner. This uses an air plasma generated with a DC potential of 310 V. The specimen is not immersed in the plasma but sits about 1 cm outside the visible glow discharge. This provides very gentle cleaning conditions. The temperature increase measured at the specimen following 1 h of plasma cleaning was just 1.1 °C. Cooling was carried out using a JEOL single tilt cooling holder, which allowed samples to be cooled between ambient and liquid nitrogen temperature. UV/ozone exposure was carried out in a Bioforce Nanosciences UV/Ozone Procleaner. This uses a UV A light source to generate ozone. This system is a generic surface cleaner and is not specifically designed for electron microscopy specimens. Specimens were placed on a pre-cleaned slide and inserted into the device. The light-source to specimen distance was approximately 15 mm.

3. Results and discussion

3.1. The effect of magnification

Microscopists understand that contamination rates generally increase with both probe current and magnification. The critical factor is the local electron flux. Fig. 2 shows the effect of magnification on the measured contamination thickness on a commercial carbon support film for a given scan duration (2 min) with a 0.155 nA probe. It is very clear that the contamination thickness increases with magnification. Increasing the magnification by a factor of five (1–5 mx) results in a 10-fold increase in the amount of contamination deposited. STEM investigations on non-corrected microscopes might typically work in <1 mx magnification regime, whereas with aberration-corrected STEM, atomic resolution is generally explored at >5 mx magnification. Thus a potentially manageable contamination rate at 1 mx of 10 nm over 2 min becomes an intolerable 120 nm at 5 mx. It is interesting to note that the plot of contamination thickness versus magnification is approximately linear. Doubling the magnification would be expected to halve both the *x* and *y* dimension of the scanned image, resulting in a reduction of the scanned area by a factor of four, and