Application of Reactive Gas Plasma Cleaning in Mitigating Contamination of Specimens during Transmission and Analytical Electron Microscopy

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Microstructural observations are not sufficient to characterize all the features which are encountered during characterization of materials. Using a combination of analytical spectroscopies such as XEDS, and EELS we can gain additional insight into the factors controlling or affecting materials properties beyond that which can be determined using standard imaging tools.

During these analytical studies focussed probes are frequently employed to determine local compositions, however, subtle processes which involve the specimen, the electron beam and any mobile species on the sample surface frequently cause the build up of hydrocarbon contamination layers.
While serving to indicate the location of the electron probe, the contamination obliterates the area of the specimen being analyzed and adversely affects all quantitative microanalysis methodologies.

A variety of methods including: UV, electron beam flooding, heating and/or cooling can decrease the rate of contamination, however, none of these methods directly attack the source of specimen borne contamination.

Research has shown that reactive gas plasmas may be used to clean both the specimen and stage for AEM, in this study we report on quantitative measurements of the reduction in contamination rates in an AEM as a function of operating conditions and plasma gases.
Example:

- The figure at the right shows the results of contamination formed when a 300 kV probe is focussed on the surface of a freshly electropolished 304 SS TEM specimen.

- The dark deposits mainly consist of hydrocarbons which diffuse across the surface of the specimen to the immediate vicinity of the electron probe. The amount of the contamination is a function of the time spent at each location. Here the time was varied from 15 - 300 seconds.
Experimental

• TEM specimens
  Electropolished 304 Stainless Steel
  Chemically polished Silicon
  Crushed Zirconolite on Holey Carbon Film

• Microscopy
  Philips CM30T at ANL Materials Science Div.
  300 kV, LaB6 Gun, 20 nm/0.7 nA probe
  RT DT Be Stage, LN₂ Cold Trap Used
  EDAX PowerMX - XEDS System
  Gatan 666 PEELS System

• Plasma Cleaning System
  Model: PC-150 South Bay Technology
  Power: 10 W, Gas Pressure 200 mT.
  Gases: nominally pure Argon & Oxygen
  mixed as needed in Model 150
To measure the rate of contamination we employed electron energy loss spectroscopy (EELS) and monitored the rate of change of the intensity of the zero loss ($I_0$) to the total integrated intensity in the spectrum ($I_T$).

This ratio is directly proportional to the local thickness of the specimen.

\[
t = \lambda \times \ln \left( \frac{I_0}{I_T} \right)
\]

\[
\lambda = \text{mean free path}
\]
Data Analysis

- Individual Electron Energy Loss Spectra are measured as a function of time.
- Spectra are then individually analyzed and the value of $t/\lambda$ is determined.
- The instantaneous contamination rate is given by $\delta (t/\lambda)/\delta T$. 

![Intensity vs Energy Loss](image1)

![Mass Thickness vs Time](image2)
Results from Electropolished 304 SS

- Untreated Specimens exhibit severe contamination

- Argon gas processing for 5 minutes @ 10 W/200 mT reduces the contamination rate ~ 50 x.

- Additional treatment of sample with pure Oxygen (5 minutes) reduces the contamination rate further to > 500x.
Comparision Results on Electropolished 304 SS

- Untreated Specimen
- After 5 minutes of Argon Processing
- After 5 minutes of additional Oxygen Processing
Successive 5 minute processing of the same specimen with Argon continuously reduces the contamination rate but does not completely eliminate the problem.

A final 5 minute treatment in pure Oxygen always reduced the rate to lower levels. Regardless of the length of time of Argon processing.
• Initial Contamination rates of Silicon are less than 304SS

• Argon alone is very efficient in Silicon

• Oxygen has a small but measurable effect and always reduces the contamination rate, however, the difference is much less than in 304 SS
Contamination of the Zirconolite is due to suspension of crushed mineral in solvents. A “drop” of the crushed mineral is then deposited on the H.C. film to make the sample. This leaves organic residue on the sample and the Holey Carbon film.

Argon treatment greatly reduces the contamination rate, a final treatment in pure Oxygen further decreases the problem.
A “drop” solvent is deposited on the H.C. film to make the sample. This leaves organic residue on the Holey Carbon film, which is now the major source of the hydrocarbon deposits.

Long processing (~15 minutes) can effect the Holey Carbon support film and should be avoided.

Results from Holey Carbon Films

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**Contamination on Holey Carbon Films**

- **As received**
- **5 Min Argon Plasma**
In all cases tested the most effective cleaning occurred when a two-step process was carried out.

5 Min pure Argon followed by 5 Min pure Oxygen

This was more effective and reduced the contamination rate more than using a Ar/O$_2$ mixture (50/50)
Using a conventional thermocouple in an AEM stage, the temperature rise of a SS sample and stage was measured as a function of input power to the plasma.

Compared to a 150W flood lamp, the increase in temperature is insignificant ~ 5-6°C for the typical conditions used for cleaning (10 W @ 5 min).
Using XPS deposition of surface layers of material, were detected. This occurs only when cleaning conditions are set incorrectly.

Using XEDS & EELS in the AEM no measurable redeposition of plasma chamber materials or oxide formation was observed on the Silicon or SS samples.

Analytical Results

Silicon Sample after Ar & O₂ Processing

Surface Composition

- Composition (at. %)
- d.c. Bias Voltage (V)
- Energy Loss (eV)
- Photodiode Counts
- O₁s = 532 eV

Silicon Sample after Ar & O₂ Processing
XPS Results on Silicon as a function of DC Bias
Conclusions

• Reactive Gas Plasma’s are an effective means of mitigating the problem of hydrocarbon contamination in an AEM for a wide range of specimen types.

• When using a capacitive coupled parallel plate geometry, optimal conditions are centered around a power rating of 10 W and a gas pressure of 200 mT at a DC bias ~ 30-40 V.

• The best results are obtained by using a 2 step processing of pure Argon followed by pure Oxygen for a time interval of 5 minutes each.

• No AEM detectable species are deposited on the specimen under cleaning conditions.

• Improperly setting DC bias will sputter material off the r.f. antenna.