Reactive Gas Plasma Specimen Processing for Use in Microanalysis and Imaging in Analytical Electron Microscopy

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Introduction

- *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.*

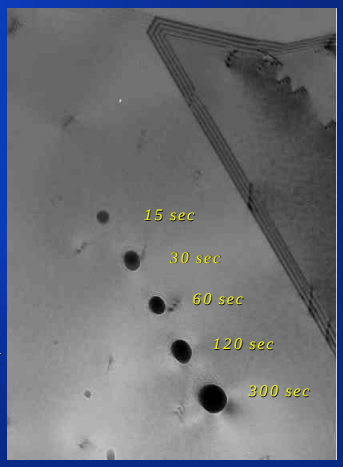
Background

- 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. (see reference 1)
- 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. (reference 2)

Reactive Gas Plasma Processing Applications to Analytical Electron Microscopy

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

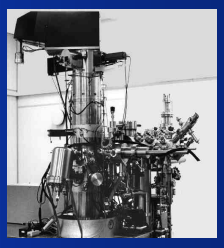
- *TEM specimens*
  - *Electropolished 304 Stainless Steel*
  - *Chemically polished Silicon*
  - *Crushed $CaZrTiO_3$ on Holey Carbon Film*
  - *Si/Cr/Au Multilayer Ion-Milled*

- *Microscopy*
  - *Philips CM30T at ANL Materials Science Div.*
  - *300 kV, LaB6 Gun, 20 nm/0.7 nA probe*
  - *RT DT Be Stage, LN_2 Cold Trap Used*
  - *EDAX PowerMX - XEDS System*
  - *Gatan 666 PEELS System*

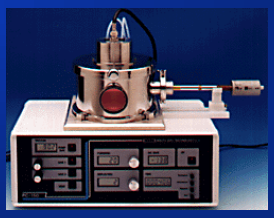
  - *ANL-VG HB603Z AAEM*
  - *300 kV, CFEG, 1nm/1nA probe*
  - *RT DT Be Stage, No LN_2 Cold Traps*
  - *Oxford/Link XEDS System*
  - *VG EELS system*

- *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*
  - *Pumping: Conventional mechanical roughing pump*

Philips CM30T



VG HB 603Z



SBT PC 150

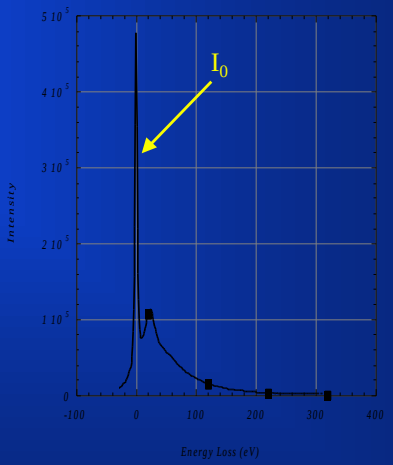
Experimental

- 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.

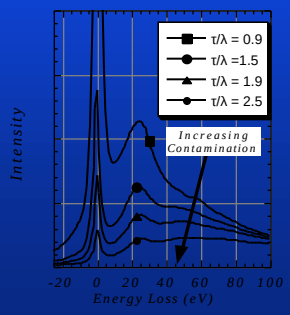
$$t = \lambda * \ln (I_o / I_T)$$

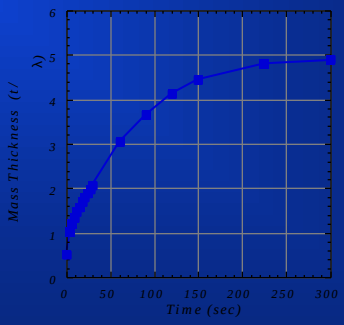
λ = mean free path



Data Analysis

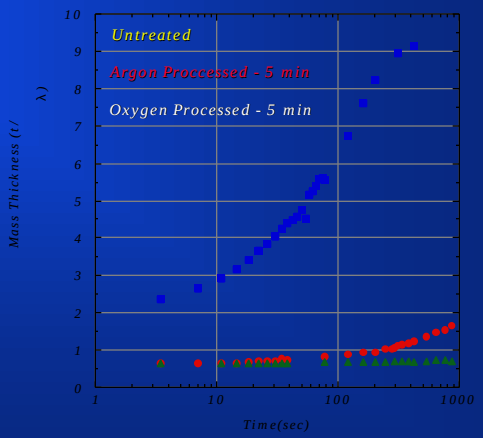
- *Individual Electron Energy Loss Spectra are measured as a function of time*
- *Spectra are then individually analyzed and the value of t/λ is determined.*
- *The instantaneous contamination rate is given by δ (t/λ)/δT*





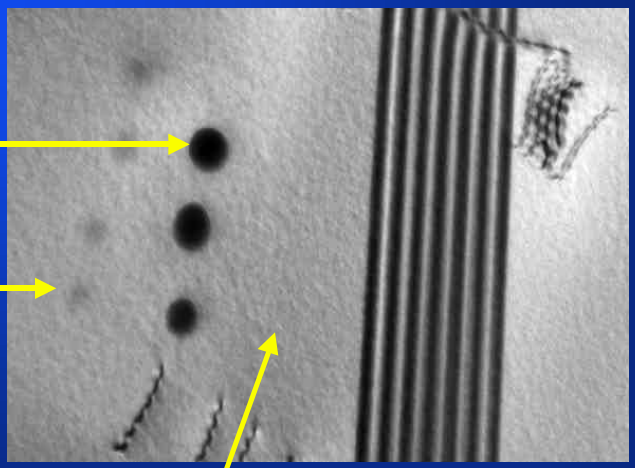
Results from Electropolished 304 SS

- Untreated Specimens exhibit severe contamination
- Argon gas processing for 5 minutes @ 10 W/200 mT reduces the contamination rate to less than 1/50 th of the untreated sample.
- Additional treatment of sample with pure Oxygen (5 minutes) reduces the contamination rate further to less than 1/ 500 th of the untreated sample.

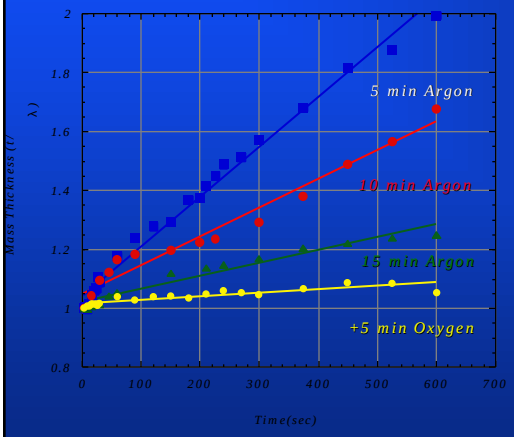


Comparision Results on Electropolished 304 SS

- Untreated Specimen
- After 5 minutes Argon Processing
- After 5 minutes of additional Oxygen Processing



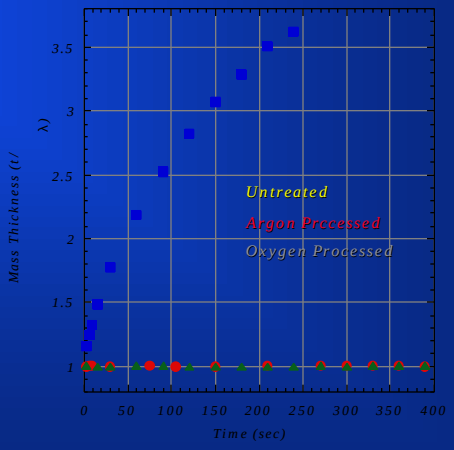
Results from Electropolished 304 SS



- 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 treatement in pure Oxygen always reduced the rate to lower levels. Regardless of the length of time of Argon processing

Results from Chemically Polished Silicon

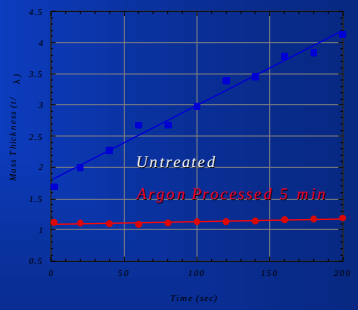
- Initial Contamination rates of Silicon are less than 304SS
- Argon alone is very efficient in Silicon
- Oxygen has a small but measurable effect and always reduces the contamination rate, however, the difference is much less than in 304 SS



Results from Crushed Zirconolite on Holey Carbon

- 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 leave 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.

Crushed Zirconolite on Holey Carbon



Results from Holey Carbon Films

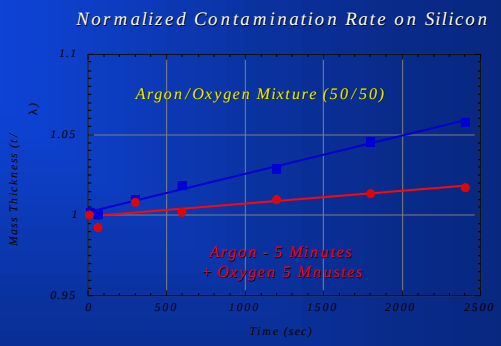
- Contamination of theHoley Carbon is due to suspension of crushed mineral in solvents. A “drop” of the crushed mineral is then deposited on the H.C. film to make the sample. This leave organic residue on the sample and the Holey Carbon film.
- Long processing (~ 15minutes) can effect the Holey Carbon support film and should be avoided.

Gas Mixing Results

- In all cases tested the most effective cleaning occured when a two step process was carried out.

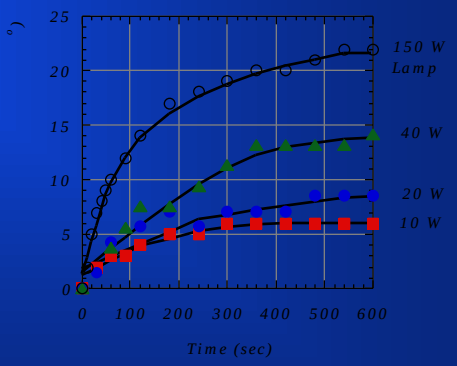
  5 Min pure Argon followed by
  5 Min pure Oxygen

- This was more effective and reduced the contamination rate more than using a Ar/O_2 mixture (50/50)



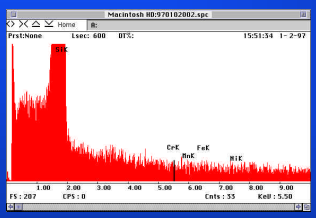
Heating Effects of the Plasma

- 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).

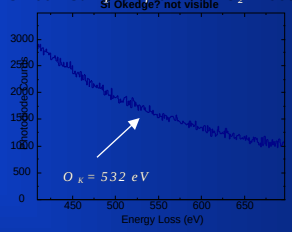


Analytical Results

Silicon Sample after Ar & O_2 Processing



Silicon Sample after Ar & O_2 Processing



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

•Improperly setting DC bias will sputter material off the r.f. antenna. (reference 3)

Summary of Results & 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. (reference 2)

- 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 ~ 40 V.

- The best results are consistently obtained by using a 2 step processing of pure Argon followed by pure Oxygen for a time interval of 5 minutes each. Mixing Ar/O is not as efficient as using seperate gas treatments.

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

- Reactive gas cleaned samples recontaminate slowly in conventional vacuum microscopes (CM30), however, the onset is delayed in UHV instruments (HB 603Z).

References

- Hren, Introduction to Analytical Electron Microscopy, Plenum Press, (1979), Chptr. 18

- Simultaneous Specimen and Stage Cleaning Device for Analytical Electron Microscopy US Patent # 5,510,624 - Argonne National Laboratory and the University of Chicago (1996)

- Zaluzec, Walck, Grant, Roberts. 1997 Spring MRS Symposium - San Francisco

Acknowledgements

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