AFRL-RX-WP-TP-2008-4022

ADVANCED TEM SAMPLE PREPARATION USING LOW ENERGY (PREPRINT)

F.J. Scheltens, R. Wheeler IV, and K. Mahalingam

UES, Inc.

NOVEMBER 2007

AIR FORCE RESEARCH LABORATORY
MATERIALS AND MANUFACTURING DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YY)*
November 2007

2. REPORT TYPE
Conference Paper Preprint

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE
ADVANCED TEM SAMPLE PREPARATION USING LOW ENERGY (PREPRINT)

5a. CONTRACT NUMBER
F33615-03-C-5206

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
62102F

6. AUTHOR(S)
F.J. Scheltens, R. Wheeler IV, and K. Mahalingam

5d. PROJECT NUMBER
4347

5e. TASK NUMBER
13

5f. WORK UNIT NUMBER
43471301

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

UES, Inc.
4401 Dayton-Xenia Road
Dayton, OH 45431-1894

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory
Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, OH 45433-7750
Air Force Materiel Command
United States Air Force

10. SPONSORING/MONITORING AGENCY ACRONYM(S)
AFRL/RXLMP

11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)
AFRL-RX-WP-TP-2008-4022

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES
Conference paper to be published in the Conference Proceedings of the Materials Research Society Symposium.

PAO Case Number: WPAFB 07-0620, 04 Dec 2007. Paper contains color.

14. ABSTRACT
The recent advent and availability of aberration-corrected (S)TEM instruments means that more information about samples are visible, and important aspects of their chemistry, atom locations, surface properties, and microstructure are quantifiable in both 2D and 3D. Surface damage and unintended ion implanted layers incurred during ion beam-assisted TEM sample preparation are being more deeply recognized as artifacts limiting the information that can be obtained using analytical electron microscopy. Both the quality and quantity of scientific and technological results are impacted by artifacts because deleterious surface layers are often a significant fraction of total sample thickness, and also because more samples of more materials are being made by ion beam-assisted techniques. After initially being prepared using conventional broad-beam or focused ion-beam assisted milling, samples that have been post-processed with low voltage Ar ion beams show significant reductions in surface amorphous layer thickness, and also alteration of implanted Ga layers.

15. SUBJECT TERMS
TEM, electron microscopy, ion beam, milling, FIB

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT:**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** (Monitor)
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			David W. Mahaffey
Unclassified	Unclassified	Unclassified	SAR	12	**19b. TELEPHONE NUMBER** *(Include Area Code)* N/A

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18

ABSTRACT

The recent advent and availability of aberration-corrected (S)TEM instruments means that more information about samples are visible, and important aspects of their chemistry, atom locations, surface properties, and microstructure are quantifiable in both 2D and 3D.

Surface damage and unintended ion implanted layers incurred during ion beam-assisted TEM sample preparation are being more deeply recognized as artifacts limiting the information that can be obtained using analytical electron microscopy. Both the quality and quantity of scientific and technological results are impacted by artifacts because deleterious surface layers are often a significant fraction of total sample thickness, and also because more samples of more materials are being made by ion beam-assisted techniques.

After initially being prepared using conventional broad-beam or focused ion-beam assisted milling, samples that have been post-processed with low voltage Ar ion beams show significant reductions in surface amorphous layer thickness, and also alteration of implanted Ga layers. Benefits and examples of the use of low energy Ar beam milling, and its enhancement to sample quality and analytical information content are presented.

INTRODUCTION

Within the last two decades, Focused Ion Beam (FIB) systems incorporating Ga beams of up to 50kV have become commercially available and have been used to make samples for TEM analysis. In many cases, up to 60% or more of the samples produced at a given laboratory may be prepared using a FIB system. The extraction and precise thinning of TEM samples with accuracy and site-specificity is a distinct and important advantage [1-4].

In parallel, though somewhat subsequent to the development of FIB systems, advances in aberration-corrected (S)TEM imaging resolution, monochromation, and increased computerization of analytical methods have been made during the last decade [5]. Techniques such as Electron Energy Loss Spectroscopy (EELS) and High-Angle Annular Dark Field (HAADF), used for elemental identification and quantification, and energy-filtered or Z-contrast imaging are now in common use in many laboratories. These improvements in the analytical capability and sensitivity of modern microscopes have necessitated that the study and elimination of artifacts incurred during sample prep once again be emphasized. For example, artifacts of sample thinning with a Ga ion beam include surface amorphization, Ga implantation, and the generation of crystallographic defects [4, 6-9]. It is important to note that samples prepared by conventional polishing and broad-beam ion thinning methods can also exhibit surface damage [7], and that disordered surface layers such as thin native oxides have been shown to contribute significantly to surface plasmon excitations in low-loss EELS [10].

Though effects of surface damage can be lessened by a variety of means, low energy (< 1 kV) inert ion bombardment is perhaps more straightforward to implement [6-9, 11]. For crystalline samples, the key is to progressively thin or remove surface damage while the material underneath remains unaltered. Damaged surface layers may be a substantial fraction of the total sample thickness, so reducing them significantly in thickness yields samples suitable for a variety of analytical techniques. For example, analysis using EELS and HREM require samples to be thinned to the single-scattering regime and to meet weak phase object criteria, respectively. The challenge of sample prep is compounded by the use of small (~30 x 15 μm) FIB liftout samples, in that post-FIB damage removal based on broad-beam ion milling incurs risk of re-deposition due to sputtering of supporting grid material or undesired parts of the sample itself. The ability to focus and selectively target the milling beam is therefore desirable.

In this paper, the benefits of low energy Ar milling for removing amorphous surface layers and improving microscopy results are elucidated.

EXPERIMENT

TEM and SEM samples of several important materials classes were used in this study. These include semiconductor Si and InAs/GaSb, a Ni-based superalloy, and a metal foil of Ag with a thick, intentionally produced surface oxide.

Samples of Si milled with a 30kV Ga beam were first prepared to assess the surface chemistry and damage associated with ion beam thinning. Chemical analysis of the Ga beam milled surface was conducted using a X-ray Photoelectron Spectroscopy (XPS) system with a spot size nominally 350 μm in diameter. To best prepare FIB liftout samples for subsequent TEM-EDS analysis, a capping layer of Au was deposited to protect and preserve the as-milled sample surfaces from further alteration by the Ga beam. Samples for the other TEM analyses were prepared either by the FIB *in situ* liftout technique, or as noted, by conventional polishing in conjunction with broad-beam Ar ion milling. Post-prep low energy Ar ion milling was conducted at ion accelerating voltages of 900 and 500V. HREM and STEM imaging and microanalysis was conducted at 300 and 200kV in field-emission instruments.

Blanket oxidation of the Ag sample was accomplished by immersion in a 75% Ar-25% O plasma for 15 min. After milling at 900V for 15 hr at 15 degrees incidence, SEM imaging and Energy-Dispersive x-ray Spectroscopy (EDS) was conducted at 2 and 10kV, respectively.

DISCUSSION

Surface analysis and FIB *in situ* liftout experiments

The results of XPS analysis of the as-FIB'ed surface are shown in Table I [12], which shows that Ga remains at and near the surface of the FIB-processed area along with C, Al, Si, and complex hydrated oxides of several compounds. A slight rise in the Ga signal was observed at ~10 nm below the surface and is attributable primarily to surface implanted Ga^0 and Ga oxide formation. That complex surface chemistry is observed after Ga beam milling is reasonable and not unexpected in the absence of vacuum transfer between instruments [13]. One must then expect that (S)TEM or other analytical results may be affected if the presence of disordered surface layers containing a complex mixture of such constituents is not fully considered.

Table I. High energy resolution XPS results for the surface of the Si sample after 30kV Ga ion beam milling [12].

Element	Element at. %	Component Binding Energy (eV) Corrected	Component at. %	Component Identity
C 1s	25.11	285.00	19.43	C - C
		286.59	1.69	C - O
		288.95	2.00	C - O - C (=O) - C
O 1s	47.99	531.01	2.33	Al2O3 • 0.30 Ga2O3 • 2.68 H2O
		532.55	45.66	SiO2 • 0.35 H2O, C - O - C (=O) - C, C - O
Si 2p	24.43	99.09	7.39	Si
		103.29	17.04	SiO2 • 0.35 H2O
Al 2p	0.67	72.68	0.29	Al
		75.59	0.71	Al2O3 • 0.30 Ga2O3 • 2.68 H2O
Ga 3d	0.50	18.72	0.29	Ga
		21.22	0.21	Al2O3 • 0.30 Ga2O3 • 2.68 H2O

Results of subsequent imaging and TEM-EDS analyses before and after low energy Ar milling are shown below. The application of low energy Ar milling has reduced the thickness of the surface damage (amorphous) layer from 25.0 to 6.25 nm, and the EDS data shows evidence of the reduction of surface Ga.

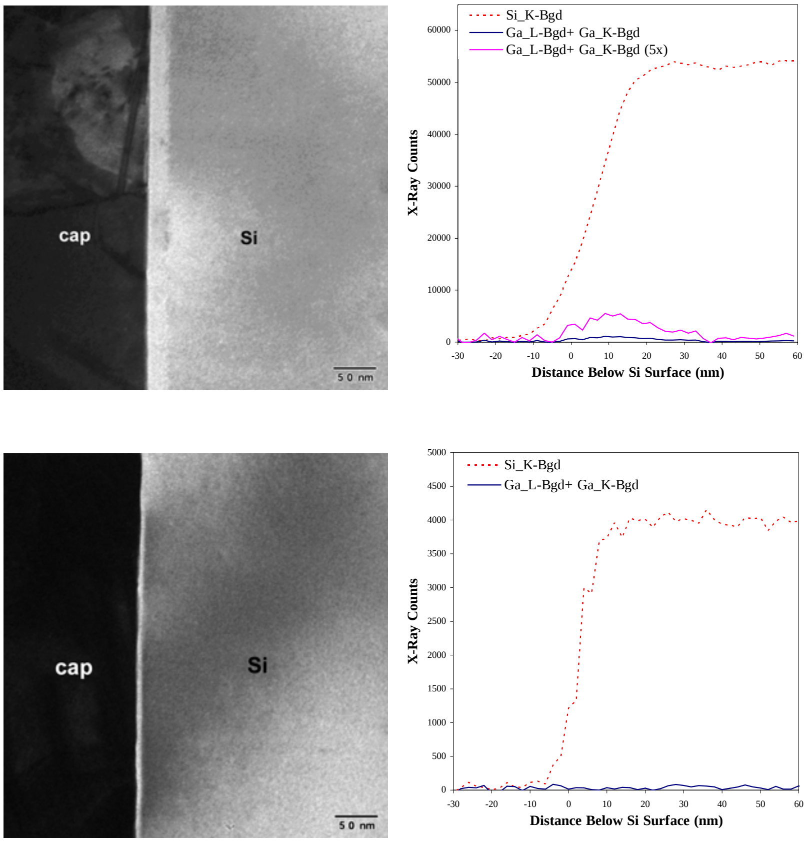

Figure 1a-d. TEM-BF images and TEM-EDS profiles showing background-subtracted Si-K and total Ga-L + Ga-K x-ray counts as a function of distance in FIB liftout samples of Si, *before* (a,b) and *after* (c,d) low energy Ar milling a 35 x 35 um region for 25 min at 900V, respectively.

The removal of thin, damaged surface layers necessitates use of relatively slow milling rates to avoid over-thinning the sample. AFM was used to measure these rates on Si (100) wafers samples, and to show the shape of the milled areas, as presented in Figure 2.

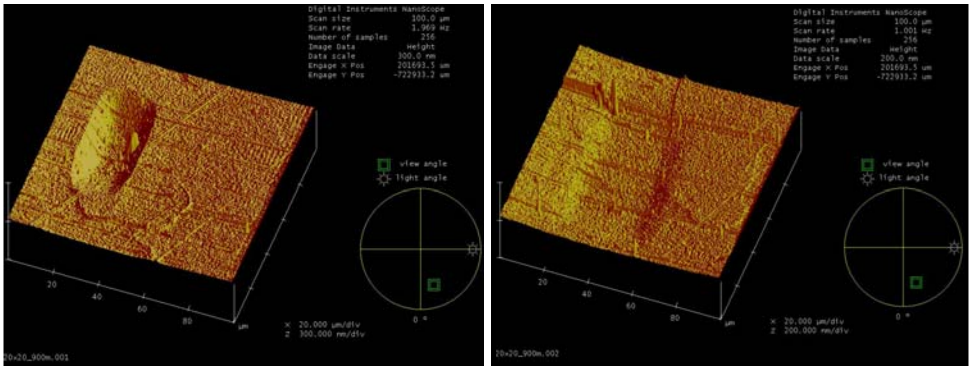

Figure 2a-b. Si sample topography after targeted 900V Ar milling. a) 20 x 20 µm area, b) 40 x 40 µm area. Milling rates were measured to be 7.7 and 2.0 nm/min, respectively.

Conventionally prepared samples (Ni-based superalloy and InAs/GaSb)

Samples prepared by polishing and broad-beam ion milling at higher voltages, or samples which have surface oxidation due to a period of storage, are also amenable to low energy Ar milling to improve surface quality and microscopy results. Successful results have been obtained for a polished and broad-beam milled sample of Ni-based superalloy, as shown in Figure 3. The progressive improvement in HREM clarity and the reduction of surface mottling, related to the smoothing of topography is observed. Figure 3 shows that the progressive reduction of surface damage can be monitored intermittently during low energy milling by using HREM imaging in conjunction with Fast-Fourier Transforms (FFTs), which show the periodicities conveyed by the objective lens in phase contrast imaging. The FFTs show significant reduction of the ‘diffuse halo’ arising from amorphous material, as it is reduced in thickness from the sample top and bottom surfaces. By reducing the Ar milling beam energy, a steady-state operating point is sought where the rate of damage removal outweighs the potential for creating new damage.

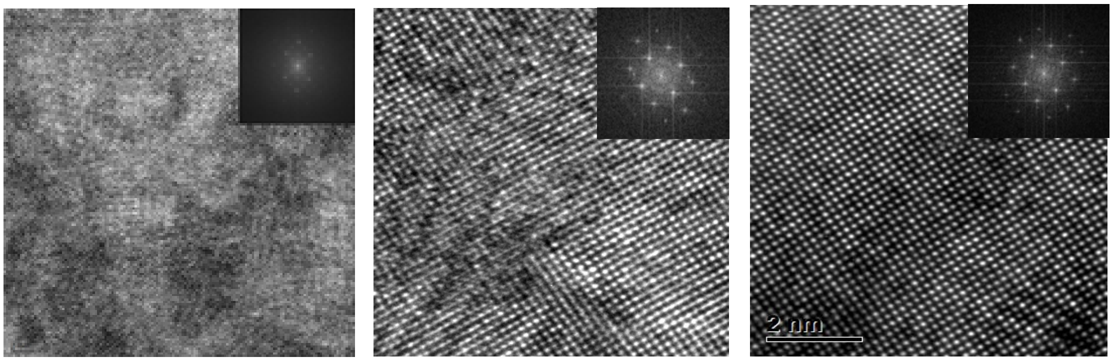

Figure 3a-c. Improved HREM of a Ni-based superalloy sample after successive applications of low energy Ar milling for 20 min per side at 15 and 10 degrees angle of incidence, respectively. a) as-received (lower magnification), and b) after 900V, and c) after 500V.

The ion beam assisted preparation of III-V compound semiconductors is difficult due to thermal degradation as well as sensitivity to ion-induced collision-cascade damage. In the InAs/GaSb multilayer sample shown in Figure 4, surface damage has been significantly reduced by milling with progressively reduced Ar ion beam energies and sample cooling.

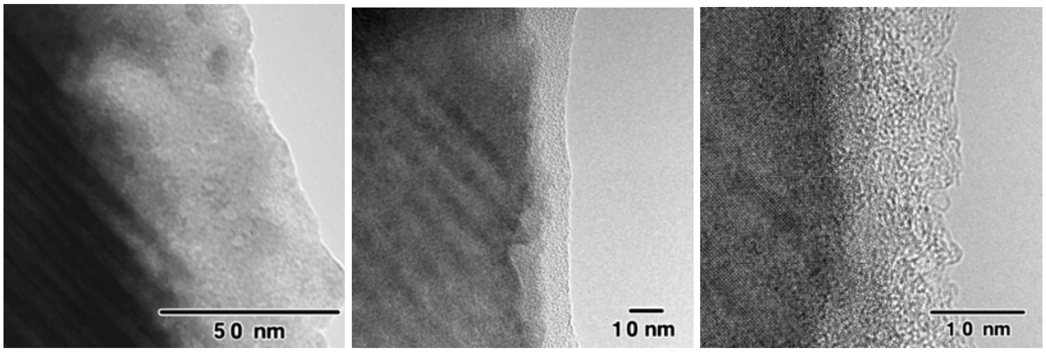

Figure 4a-c. Reduction of surface damage layer in a InAs/GaSb multi-layer sample after low energy Ar milling, a) at 900V, and b-c) subsequently at 500V. The sample was cooled to approximately -160C during milling.

Oxide removal from a metal surface

To study the effect of low energy Ar milling for surface smoothing and removal of an overlayer of thick oxide, a relatively rough sample of Ag foil was intentionally oxidized by immersion in a 75% Ar - 25% O plasma for 15 min. The oxide was subsequently milled in a 50 x 50 μm targeted region for 15 hr at 900V accelerating voltage, at 15 degrees angle of incidence. Results of SEM secondary electron imaging and EDS spectra comparing the as-received (region 1), with the area that received the targeted milling (region 2) are presented in Figure 5a-b. For statistical confidence, one million counts were collected in each spectrum, that were then normalized over the energy range 0 to 10 keV. The EDS comparison shows that Ag-oxide was reduced in thickness by Ar milling.

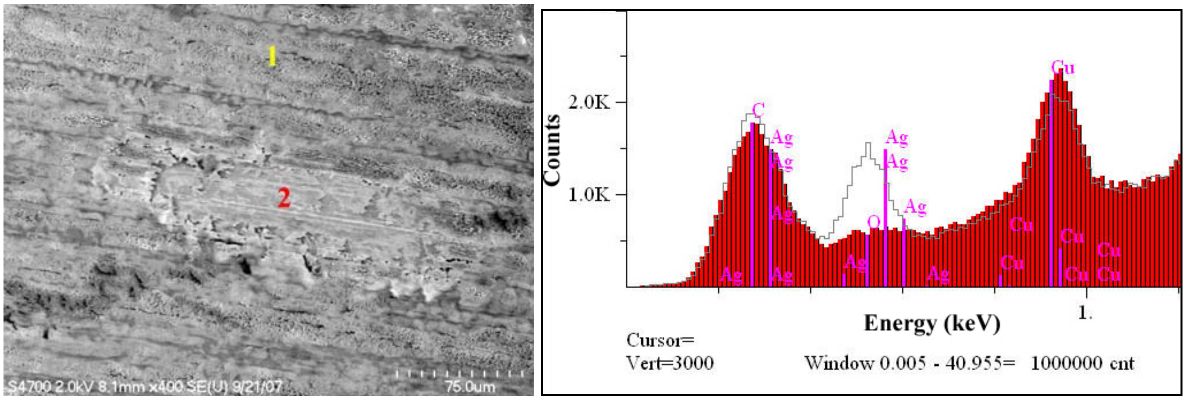

Figure 5a-b. a) SE image of the Ag foil that received Ar milling, elongated due to the 15-degree angle of incidence. A localized reduction in thickness and surface smoothing has been accomplished. b) Low-energy detail of the SEM-EDS normalized overlay spectra of as-oxidized (gray line, from region 1), and as-milled (red bars, from region 2) regions. The reduction in the O peak is due to Ag-oxide removal. The Cu peak arises from the sample holder.

CONCLUSIONS

Surface damage with complex chemistry is shown to arise when ion-assisted preparation methods are used to produce samples for analysis by (S)TEM. Considering recent progress in imaging and analytical resolution, and to facilitate further scientific and technological advance, sample preparation artifacts need to be tightly controlled to avoid spurious results. In this work, low energy Ar ion bombardment was used to reduce the thickness of ion-damaged surface layers, and to reduce residual Ga, resulting in significant improvement to results attainable via electron microscopy for several material classes. Sample surface smoothness can also be improved, and surface oxides can be thinned by selectively ion milling in targeted regions.

ACKNOWLEDGMENTS

Dr. C. Anderson of Anderson Materials Evaluation, and Y. Zhai of Ohio State University are gratefully acknowledged for XPS and AFM measurements, respectively.

REFERENCES

1. E.C. Kirk et al, Inst. Phys. Conf. Series, **100**, 501 (1989).
2. R.J. Young et al, in *Specimen Preparation for Transmission Electron Microscopy of Materials II*, ed. R. Anderson, Mater. Res. Soc. Symp. Proc. **199**, Pittsburgh, PA, (1990), pp. 205-216.
3. D.P. Basile et al, in *Specimen Preparation for Transmission Electron Microscopy of Materials III*, ed. R. Anderson, B. Tracy, and J. Bravman, Mater. Res. Soc. Symp. Proc. **254**, Boston, MA, (1992) pp. 23-41.
4. R. Anderson and S. Klepeis, in *Introduction to Focused Ion Beams*, edited by L. Giannuzzi and F. Stevie, (Springer, New York, 2005) pp. 173-200; T. Kamino et al, ibid., pp. 229-245.
5. P.E. Batson et al, Nature, **418**, 617 (2002).
6. N.I. Kato, J. Electron Microsc., **53**, 451 (2004).
7. A. Barna, Mater. Res. Soc. Symp. Proc. **254**, Boston, MA, (1992), pp. 3-22; Micron, **30**, 267, (1999).
8. D. Barber, Ultramicroscopy, **52**, 101 (1993).
9. C.A. Volkert et al, MRS Bulletin, 32, pp. 389-395, (2007); J. Mayer et al, ibid., pp. 400-407; W. MoberlyChan, ibid., pp. 424-432.
10. K.A. Mkhoyan et al, Ultramicroscopy, **107**, 345 (2007).
11. A. Genc et al, Proc. Microscopy & Microanalysis, Ft. Lauderdale, FL, CD1520 (2007).
12. C. Anderson (private communication).
13. A. Ferryman et al, Surf. Interf. Anal., **33**, 907 (2002).