APPLICATIONS OF PLASMA CLEANING FOR ELECTRON MICROSCOPY OF SEMICONDUCTING MATERIALS

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ABSTRACT

As semiconductor device sizes continue to decrease, the degree of accuracy needed for electron microscopy and microanalyis of such materials increases. To achieve such accuracy, small electron probes with high beam currents are needed. The combination of these two factors results in an increase in the amount of carbonaceous contamination formed on the specimen under the electron beam. Recently, the use of low energy plasmas has been shown to be effective in preventing such contamination from occurring [1-7], For TEM, the simultaneous placement of the specimen holder and specimen into such a plasma for short periods of time results in the ability to hold a converged probe on the specimen for analysis without contamination becoming an problem. Furthermore, in this presentation we show that existing contamination from prior TEM analysis can be removed from the specimen by plasma cleaning. The benefits of plasma cleaning are not solely limited to TEM. SEM specimens, as well as SEM specimen holders, aperture strips, tweezers and other electron microscopy accessories can readily be inserted into the plasma chamber for cleaning.

INTRODUCTION

To achieve optimum results during electron microscopy of semiconducting materials, it is necessary to have a clean, well-prepared specimen. It is essential to prepare specimens without significantly altering their microstructure or composition. Current specimen preparation techniques (mechanical polishing, electrolytic thinning, ion beam milling) often introduce amorphous damage layers, residual surface layers and specimen contamination. This specimen borne contamination can severely limit the ability to perform accurate electron microscope analysis of these materials, especially as specimen areas of interest decrease in size.

This hydrocarbon contamination may come from several sources during specimen preparation: inadvertent touching of the specimen or specimen holder, backstreaming of oil from an oil diffusion pumped ion milling system, chemicals used during electrolytic thinning, or through the application of adhesives and/or solvents. Even when great care is taken to clean the specimen, standard methods are not fully successful. In addition to contamination from the specimen, contamination from the TEM column or specimen holder will also affect analysis.

Plasma cleaning of specimens prior to electron microscopy has proven to be a highly effective method of mitigating specimen borne contamination. In plasma processing, various gases react chemically with different materials. An oxygen plasma is highly effective in removing hydrocarbon contamination. The disassociated oxygen created by the plasma chemically reacts with the hydrocarbon material present on the object being processed, converting it to CO, CO_2, and H_20, which are evacuated by the vacuum system [8]. Alternative gases can be substituted to assist in removing various other types of contamination or to selectively etch individual elements within a specimen.

For the removal of hydrocarbon contamination, a mixture of 25% oxygen and 75% argon was found most suitable [9]. It was determined that 25% oxygen would be sufficient for the chemical reduction of hydrocarbons, while remaining less volatile for laboratory safety. Following the selection of the 25% oxygen concentration, the balance gas was chosen. The requirements were for an inert gas that is easily ionized. Argon became the ideal candidate since it does not chemically

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react with the specimen and is commonly accepted for the conventional ion milling of TEM specimens. For the sake of convenience a blended oxygen/argon process gas, contained in a single cylinder, is used for general cleaning.

For plasma processing, the gas plasma is created within a cylindrical chamber where the object being plasma cleaned is contained, as shown in Figure 1. Gas dynamics analysis indicates an even distribution of plasma within the chamber and around the object being processed. A high frequency (HF) antenna, located external to the chamber, inductively couples the oscillating electromagnetic field through the quartz chamber walls and generates the plasma. A critical aspect of this low-energy form of plasma creation is that no components (i.e., electrodes) are located within the plasma, other than the objects that are being cleaned. This enables effective cleaning with negligible specimen heating and eliminates the sputtering of electrode material onto the specimen and specimen holder. In this plasma chamber design, these and a number of other factors were taken into account to ensure optimal plasma processing parameters without altering the specimen being processed. These design parameters are described in greater detail elsewhere [9].

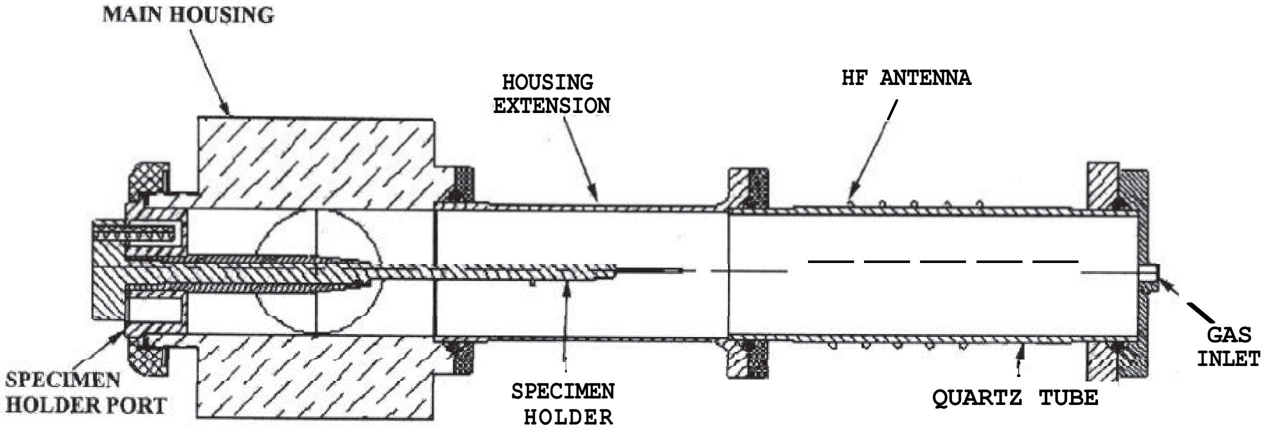

Figure 1. Plasma chamber design.

EXPERIMENT

TEM ready specimens of silicon and $SrTiO_3$ were prepared by mechanical thinning, dimpling and conventional ion milling. No extraordinary steps were performed to clean the specimens, nor were any taken to purposely contaminate them. The silicon specimens were examined using a Philips CM200-FEG at an accelerating voltage of 200 kV with a probe size of 1 nm, and fitted with an EDAX EDS system. Samples of $SrTiO_3$ and all EELS experiments were conducted on a Hitachi HF-2000 cFEG-TEM at 200 kV with a probe size of 5 nm, and fitted with a Gatan 666 PEELS system and EMiSPEC analysis software. SEM experiments were performed on a Philips XL30 FEG-SEM or a Hitachi S-4500 FEG-SEM with LN_2 cold trap, NORAN Voyager EDS system and TexSEM Laboratories electron backscattered diffraction (EBSD) system. All plasma cleaning was done with an E.A. Fischione Instruments Model 1400 Plasma Cleaner.

TEM Results

Silicon specimens were inserted into the TEM prior to plasma cleaning, and were subjected to a focused probe to initiate specimen contamination. This probe was then positioned on various areas of the specimen for decreasing lengths of time. Figure 2a is a TEM micrograph of a silicon specimen taken after the electron probe was focused on the sample. The long black streak is carbonaceous contamination formed as the probe was focused on the specimen for five minutes while the specimen drifted. After the specimen drift had stopped, the probe was positioned and held on the specimen for 5 minutes, 3 minutes, 1 minute and 30 seconds. The resulting contamination spots are seen in Figure 2a below and left of the long streak, with the spot closest to the streak formed from the 5 minute exposure. Exposure time decreases to the left with the spot furthest left in the image formed by focusing the probe for 30 second on that area of the specimen. The specimen was then removed from the TEM, and the specimen holder and specimen were plasma cleaned for two minutes using a process gas mixture of 25% oxygen in argon. The holder was then reinserted into the TEM and the probe was again focused on the specimen for five minutes. Figure 2b is the TEM micrograph taken after plasma cleaning and refocusing of the probe on the specimen. The arrow indicates the position the probe was placed for five minutes. No carbonaceous contamination is formed. Furthermore, the existing contamination spots are greatly reduced or removed completely.

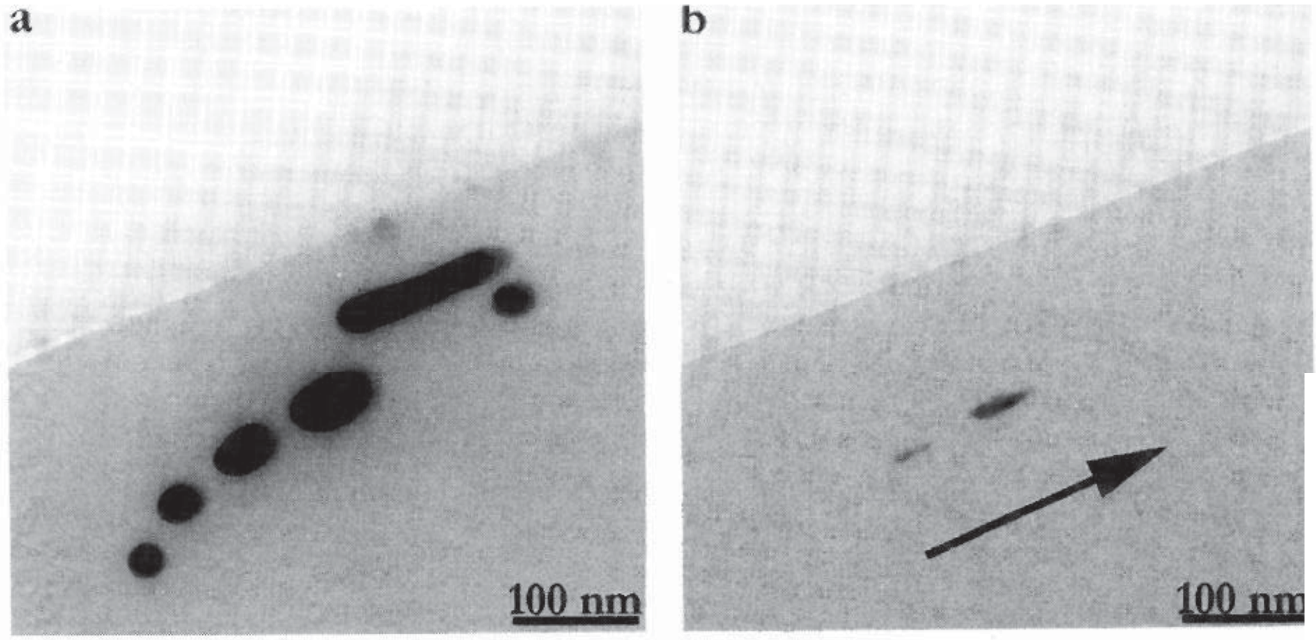

Figure 2. TEM micrographs of silicon, a) before and b) after 2 minutes of plasma cleaning.

Analytical results are likewise enhanced by plasma cleaning. Figures 3a and 3b are EDS spectra of the silicon specimen taken before and after plasma cleaning respectively. Note the elimination of carbon in the second spectra. Note also the lack of iron, nickel, chromium and other elements that would indicate sputtering of the stainless steel plasma processing chamber during plasma cleaning.

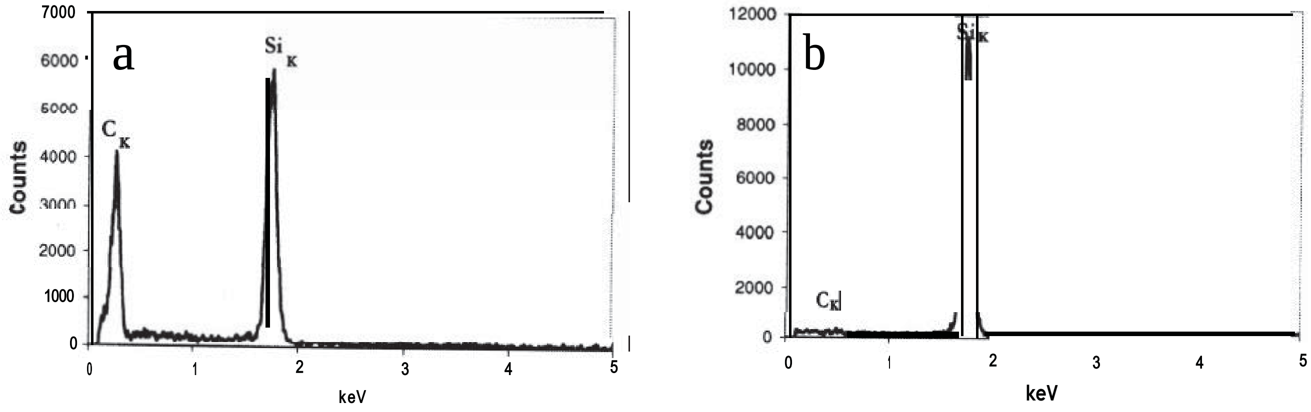

Figure 3. EDS spectra of silicon taken a) before and b) after two minutes of plasma cleaning.

Similar experiments were conducted on a number of materials, including $SrTiO_3$, stainless steel, aluminum and cubic ZrO_2. In each case the results were the same, prevention of the formation of carbonaceous contamination and the removal of existing contamination. Figures 4a and 4b are TEM micrographs of $SrTiO_3$, taken after one minute and after four minutes of plasma cleaning respectively. In Figure 4a, the black spots are again carbonaceous contamination formed prior to plasma cleaning by focusing the electron probe on the specimen for decreasing amounts of time. The largest spot was formed from a five minute exposure to the beam, while the smallest is from a 30 second exposure. After plasma cleaning for one minute, the probe was refocused for five minutes at a position to the right of the third spot in the series and the micrograph was taken. As with the silicon, no further contamination is evident. Figure 4b is the micrograph taken after an additional three minutes of plasma cleaning. The contamination spots formed prior to plasma cleaning are reduced in size or removed. In addition, in the upper left hand corner of the micrographs is a hole in the specimen. After one minute of plasma cleaning, and edge of carbonaceous debris can be seen in the interior of the hole. After the additional three minute cleaning, this too is removed.

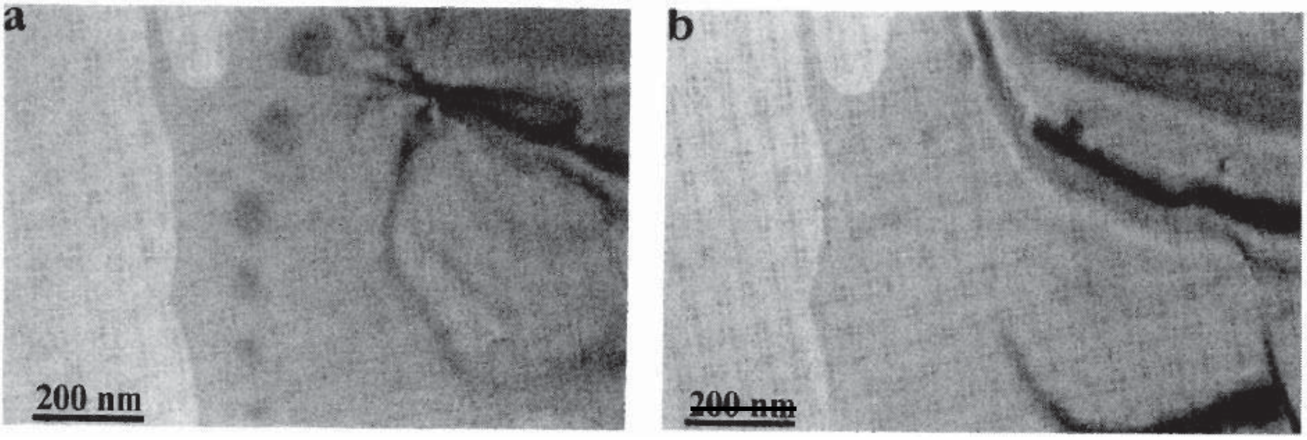

Figure 4. TEM micrographs of $SrTiO_3$ taken after a) one minute and b) four minutes of plasma cleaning.

Quantification of the effects of plasma cleaning for TEM can be determined through electron energy loss spectroscopy (EELS). In an EELS spectra, the ratio of the intensity of the zero loss peak

(b) to the total integrated intensity of the spectra (I_T/I_0) is directly related to the thickness of the specimen, t, by the relation [10]

$$t = \lambda \ln(I_T/I_0) \qquad (1)$$

where λ is the mean free path for the material being analyzed. Assuming that any changes in specimen thickness are due to the formation of contamination on the specimen, this contamination can be measured by taking EELS spectra as a function of time the electron probe is held in place on the specimen, and computing the I_T/I_0 ratio.

Spectra were collected for the silicon specimen, and the value of t/λ was determined for each as a function of time. Figure 5 are plots of t/λ versus time for the silicon specimen before and after one minute of plasma cleaning. Prior to plasma cleaning, specimen thickness increases quickly as a function of time, indicating rapid contamination of the specimen under the electron probe. After only one minute of cleaning, specimen thickness no longer varies with time. Contamination of the specimen has been eliminated.

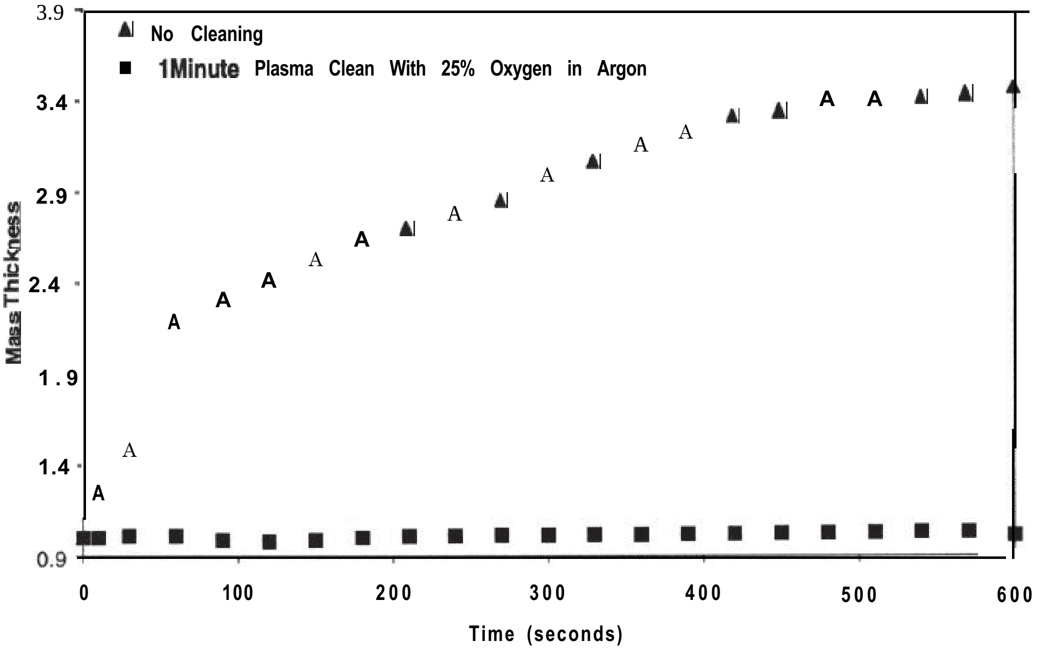

Figure 5. Variation of specimen mass thickness with time before and after plasma cleaning for silicon.

SEM Results

The most obvious improvement from plasma cleaning for SEM specimen imaging is seen in the effect of plasma cleaning SEM aperture strips and imaging at low accelerating voltages before and after cleaning. Figures 6a and b are images taken at 1 kV of gold islands on carbon, before and after 5 minutes of plasma cleaning respectively. Note the improvement in imaging resolution due to the plasma cleaning removal of existing carbonaceous debris from the 30 µm aperture.

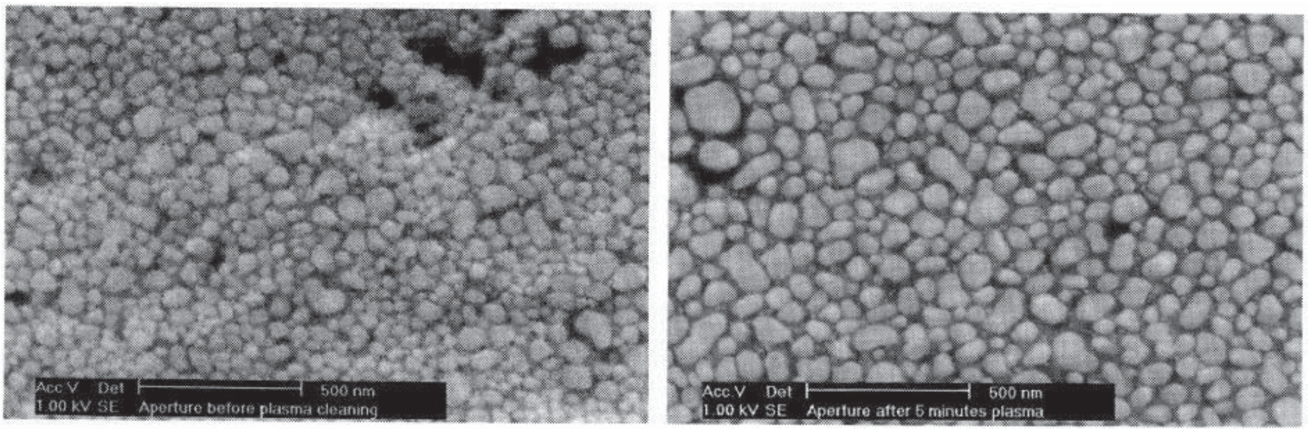

Figure 6. SEM micrographs of gold islands on carbon taken a) before and b) after plasma cleaning of the 30 μm SEM objective aperture.

Figures 7a and b are SEM EDS spectra of a specimen of pure aluminum before and after plasma cleaning. This experiment was conducted with the SEM operating in spot mode at an accelerating voltage of 30 kV with an accumulated live time of 100 seconds. In Figure 7a, a large carbon peak is seen on the spectra. After plasma cleaning the bulk specimen for two minutes in the gas mixture of 25% oxygen in argon, the carbon peak is completely eliminated from the spectra as shown in Figure 7b.

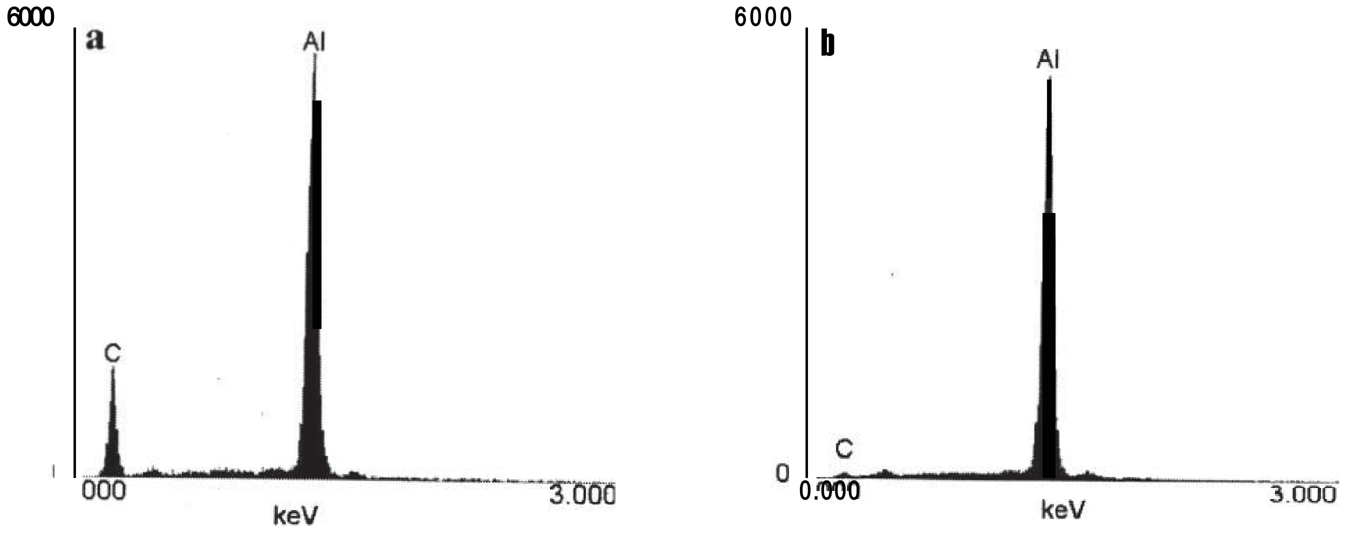

Figure 7. SEM EDS spectra of aluminum a) before and b) after two minutes of plasma cleaning.

Plasma cleaning is also of benefit for electron backscattered diffraction (EBSD). As the electron backscattered diffraction pattern (EBSP) is formed very near the specimen surface, disturbances near the surface such as specimen strains, surface roughness, and surface contamination deteriorate the quality of the pattern formed at the detector. Removal of surface contamination through plasma cleaning improves the pattern quality. Figures 8a and b are EBSPs of a bulk specimen of silicon, before and after 2 minutes of plasma cleaning respectively. Prior to the investigation, this specimen was mechanically polished in a series of steps ending with colloidal silica, and then was conventionally cleaned using methanol and acetone in series. As seen from the captured patterns, a final plasma cleaning step eliminates any residue left behind by the solvents used during the polishing and cleaning processes and improves the quality of the EBSP.

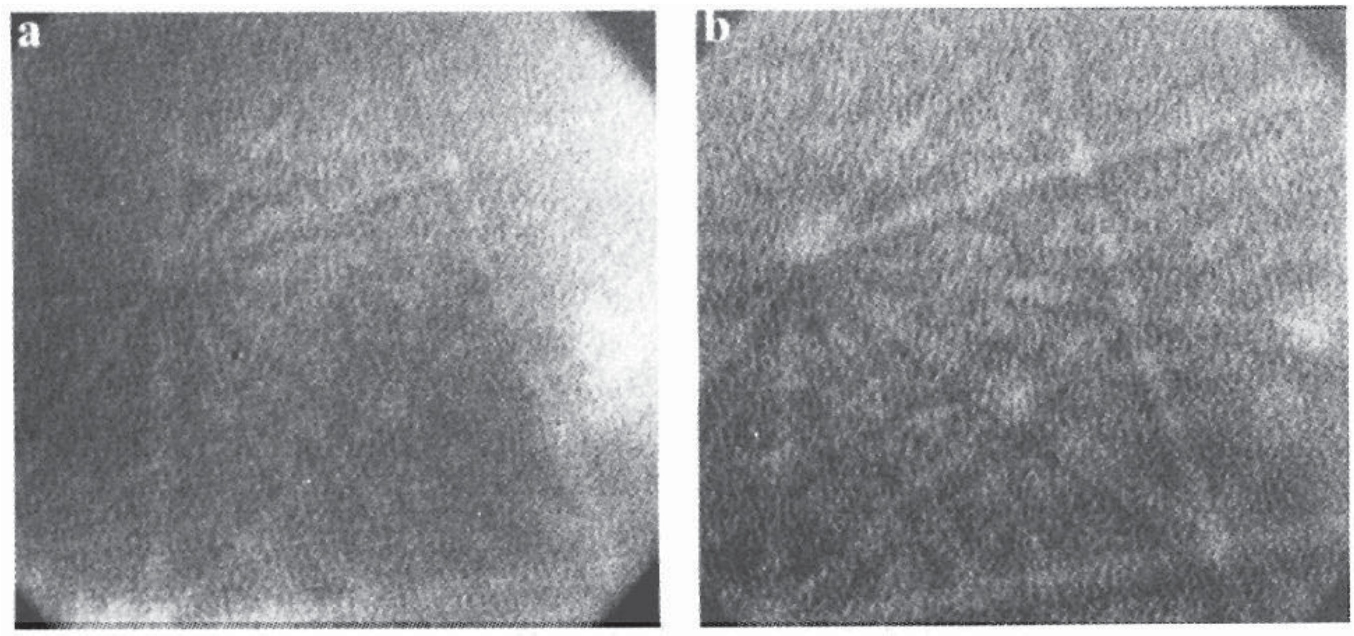

Figure 8. Electron backscattered diffraction patterns (EBSPs) of silicon a) before and b) after two minutes of plasma cleaning.

CONCLUSIONS

Plasma cleaning is an essential tool for the electron microscopy of semiconducting materials. As device size continues to get smaller, greater emphasis will be placed on site-specific analysis of small areas of specimen. To analyze these small areas effectively requires a small electron probe with high beam currents. This in turn leads to enhanced contamination of the specimen area under the probe. Plasma cleaning with a process gas mixture of 25% oxygen in argon prevents such contamination from occurring and eliminates any prior contamination from the specimen. This allows the researcher to analyze the specimen accurately for extended periods of time and enhances specimen imaging and microanalysis for both TEM and SEM.

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REFERENCES

1. P.E. Fischione, U.S. Patent Number 5,633,502 (27 May 1997).

2. J.T. Grant, S.D. Walck, F.J. Scheltons, A.A.Voevodin. Surface Science Aspects of Contamination in TEM Sample Preparation. (Mater Res Soc Symp Proc 480, Pittsburgh, PA, 1997) pp. 49-7 1.

3. S.P. Roberts, S.D. Walck, J.T. Grant, N.J. Zaluzec. Application of Reactive Gas Plasma Cleaning in Mitigating Contamination of Specimens During Transmission and Analytical Electron Microscopy. (Mater Res Soc Symp Proc 480, Pittsburgh, PA, 1997) pp. 127-136.

4. R.S. Thomas. in Preparing Specimens for Scanning Electron Microscopy and Electron Probe Microanalysis. (Proceeding of the 7th Annual Scanning Electron Microscope Symposium : Scanning Electron Microscopy, 1974) pp.84-89.

5. N.J. Zaluzec. U.S. Patent Number 5,510,624 (23 April 1996)

6. N.J. Zaluzec, B.J. Kestel, D. Henriks. Proc. Microsc. Microanal. ‘97 (1997).

7. H.W. Zandbergen, A.C.A. Delsing, C. Traeholt, A. VanVeen, J. deRoode Proceedings of the XIII International Congress for Electron Microscopy 1, 1003 (1994).

8. M. Tuszewski, J.T. Scheuer, J.A. Tobin, J. Vac. Sci. Technol. 13A, 4 (1995).

9. P.E. Fischione, J. Ringnalda, Y. Feng, T. Krekels, M. Hayles, J.O. Colijn, M.J. Mills, J.M. Wiezorek. The Use of a Cold Gas Plasma For the Final Processing of Contamination Free TEM Specimens. (Mater Res Soc. Symp Proc 480, Pittsburgh, PA, 1997) pp. 225-234.

10. D.B. Williams and C.B. Carter, Transmission Electron Microscopy, (Plenum Press, New York, 1996) p. 679.