Determination of Pore-Size Distributions in Low-k Dielectric Films by Transmission Electron Microscopy

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Abstract. This paper discusses methods of characterizing pore size distributions in low dielectric constant (low-k) films by transmission electron microscopy (TEM), comparing both conventional TEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Methods of sample preparation were tailored to protect pore structure during cross-sectional thinning allowing techniques similar to conventional mechanical polishing and low-angle ion milling. Knowledge of TEM sample thickness allows quantification of pore density distributions. TEM sample thickness and quantitative image analysis methods are discussed.

INTRODUCTION

Increased density of integrated circuits and reduced power requirements of future circuit designs force the semiconductor industry to find new lower dielectric-constant materials for insulating metal interconnects.\textsuperscript{1} The introduction of nanometer scale pores into a solid matrix is currently being considered by the industry as a means of reducing the effective dielectric response of insulating layers. However, the size, density, and connectivity of pores all play a significant role in the determination of materials properties and device performance. As processing conditions may be tailored to control the size, density and connectivity-type of pores, reliable means of pore characterization is necessary for developing optimized processing recipes. This paper discusses pertinent techniques and issues for the characterization of disordered pore distributions in low-k films by TEM. Here we focus on disordered distributions of pores; although there has also been much work on dielectric films with ordered arrays of pores, these have different requirements for TEM imaging, which have been documented.\textsuperscript{2}

Other techniques used for the characterization of pores in low-k films include X-ray diffuse scattering,\textsuperscript{3} positron annihilation lifetime spectroscopy (PALS),\textsuperscript{4} X-ray reflectivity (XRR),\textsuperscript{5} ellipsometric porosimetry (EP),\textsuperscript{6} and X-ray porosimetry (described as an XRR version of EP).\textsuperscript{7} TEM has a basic advantage over these other techniques as it can provide a real-space picture showing changes in pore distributions at a local scale that might be lost to averaging in measurements conducted over larger regions of sample area. Local density changes may cause difficulties for techniques that rely on the refinement of only a few parameters that may not be capable of adequately describing the true structural changes. The localized scale of the TEM sampling volume may also be problematic as local variations can be mistaken as reflecting the nature of the whole film when sampling is limited; thus the statistical significance of TEM sampling should always be considered. Also, sample preparation artifacts should also be considered.

SAMPLE PREP

First attempts at imaging pores in blanket-processed low-k films used samples prepared by mechanical polishing of dimpled X-sectional samples with final thinning employing a low-angle broad-beam ion mill (Gatan PIPS\textsuperscript{TM} tool, 3.5 kV Ar+ ions, 5-10 mA). This standard method for cross-sectional samples places two samples face to face making a sandwich with epoxy as the meat; this way the bulk silicon wafers protect the thin films during subsequent sample thinning. Figure 1(a) shows how the first attempts showed little sign of porosity. Also, with these samples it was very difficult to determine the low-k surface due to lack of contrast between low-k and the
epoxy used for sample preparation. A modified sample prep was developed wherein the sample surface was coated with a sputtered layer of platinum (approximately 5 nm thick), followed by a thicker (60 nm) SiO$_2$ layer deposited by chemical vapor deposition. Figure 1(b) shows that this modified prep delineates the low-k surface with a grainy platinum layer, and seals it (with SiO$_2$) preventing penetration of the epoxy so that pores remain unfilled and thus more easily imaged. Besides delineation of the low-k surface, the platinum acts as a mask to aid the flat ion milling of a porous low-k film. Away from the platinum or other slow-milling materials, dishing of the porous low-k may be observed. The Porous material mills faster because it is less dense, but since ion-milling is done at low angles, slow milling structures seem helpful by acting as a shadow-mask protecting the low-k film x-section surface.

Focused ion beam (FIB) can also be used to prepare TEM samples of porous low-k films. FIB tends to smooth out the pores on the surface of a cross-sectional sample, but this is more of a problem for secondary electron imaging as in the SEM where imaging is dependant on surface roughness. For TEM, images are a result of projection through the bulk of a sample so that as long as the bulk of the TEM sample has not been smoothed over, FIB can still allow observation of pore structures. However, it is difficult to prepare adequately thin TEM samples for imaging small pores.

One final caveat for sample preparation is that many porous low-k films may be susceptible to shrinkage due to excessive heating or ion-induced damage. Minimization of heating is most important as the sample is reaching final thickness, as this is when heat dissipation is reduced by dimensional limits.

**TEM IMAGING CONDITIONS**

For imaging with electrons accelerated in the TEM to energies of 200-300 keV, a TEM sample must be as thin as 10-200 nm. The higher energy electrons have a longer inelastic mean free path and thus are more likely to travel through the sample without imparting energy in the sample; thus higher electron energy can allow less sample damage due to heating by the electron beam. However, a trade-off is that the higher energy electrons may have an increased probability of knocking an atom out of the sample resulting in defects in crystalline materials and sputtering of amorphous or crystalline materials. Minimizing electron beam exposure is important as many of the low-k films being considered by the industry may shrink as a function of electron beam dose (or they may warp out of the imaging plane and then have the appearance of shrinking). Conventional TEM imaging can be done with lower beam currents and slightly longer camera exposures. HAADF-STEM with a small probe is inherently low-dose as the small probe used reduces total electron beam current and, since the probe is rastered over the sample, any one point on sample sees only a small fraction of the beam current averaged over time.

For conventional TEM imaging contrast can be optimized to show pores by increasing either amplitude or phase contrast. Amplitude contrast is enhanced by selecting a small objective aperture. Phase contrast is enhanced by using large defocus conditions so that Fresnel interference is observed at the edges of pores. In practice we have found that pores are more easily observed by increasing Fresnel contrast with defocus values of 600 nm to 1000 nm; amplitude contrast gained with a small objective aperture is not as helpful. Change in contrast observed with defocus is shown in Figure 2. The phase contrast approach is enhanced by the beam coherence of a FEG TEM or with more parallel illumination conditions obtained by spreading the beam before the sample.

![Figure 1.](image1.png) **Figure 1.** (a) TEM image of a porous low-k sample prepared by conventional epoxy-sandwich techniques with final thinning by ion milling. (b) The same porous low-k film with platinum and SiO$_2$ capping layers; besides capping, the sample prep method was the same for both samples.

![Figure 2.](image2.png) **Figure 2.** Same sample and position on sample (a) imaged in CTEM mode at -100 nm defocus and (b) -600 nm defocus.
Large defocus values can reduce the ability to resolve smaller pores when Fresnel contrast from neighboring pores overlap. For helium bubbles in gold, Wilkens had observed cavities as small as 1-2 nm in diameter using defocus values of 0.5 to 1.0 micrometers.

TEM magnification calibration relies on the use of standards and systematic treatment of imaging conditions including the placement of the sample in the electron-optical column (this is commonly called “Z-height” and a common operating procedure is to always set this to the goniometer eucentric position). Another important factor affecting calibration is the prevention of variable hysteresis effects in the electromagnetic lenses; many modern microscopes have routine controls set into their operation modes to reduce hysteresis problems. Routine calibration checks are important to show the variability of a particular instrument.

While less commonly available, HAADF-STEM is optimal for imaging pores in low-k. Image contrast in HAADF-STEM is more linearly related to sample mass-thickness and does not have complicated contrast reversals found in conventional TEM. Also, HAADF-STEM is inherently a low-dose technique and thus avoids sample-heating and dose-related damage induced by the high-energy electron beam. HAADF-STEM images are shown and discussed later in this paper in the section on pore distribution quantification as this technique provides data more suitable to software-based image analysis.

TEM tomography is a technique that can produce a three-dimensional rendering of the structure and distribution of larger pores in polymer films, but current methods are limited in spatial resolution to length-scales of approximately 5 nm.

**TEM SAMPLE THICKNESS**

Gidley et al. discussed the difficulties involved in quantitative analysis of pore distributions from TEM data. The problem involves relating the 2-dimensional (2-D) image to 3-dimensional (3-D) structure of the TEM sample. Figure 3 shows that a thin sample with a high pore-density could give a similar image to that of a thicker sample with lower pore-density. Quantitative analysis of pore density distributions thus requires knowledge of the TEM sample thickness.

Figure 3. Cartoon showing how a 2-D image (c) could be formed by the projection of either (a) a thin TEM sample with a high pore density, or (b) a thicker TEM sample with a lower pore density.

Furthermore, TEM sample thickness determines the ability to observe pores of different sizes. Figures 4 and 5 illustrate how a TEM sample thickness should be near the same as the pore diameter measured. If the TEM sample is thinner than the pore radius, then many pores will be sectioned away from center and appear to have a reduced size as shown in Figure 6.

Figure 4. Small pores require thinner samples. (a) a thick region of a sample with small pores can show changes in density through the sample height, but (b) a TEM sample with thickness near the pore-size length-scale is required to better show pore size, shape and distribution.

Figure 5. Large pores in low-k imaged from (a) a region of sample considerably thinner than the average pore diameter and (b) from a region of the TEM sample thicker than the average pore diameter.
If the TEM sample is significantly thicker than the average pore size, then smaller pores will be lost due to overlap and the projected image will appear similar to that of an amorphous film that does not have pores. For pores larger than the TEM sample thickness, many of the pores will be sectioned away from the pore center and will therefore appear smaller than the true pore diameter as shown in Figure 6. However, 50% of pores observed will show radii that are within 86% of the actual value. The distribution of observed fractional pore sizes is skewed towards one by the geometry of the sphere. The effects of TEM sample thickness are more complicated if one considers a broad range of pore sizes, and thus it can be helpful to record images from TEM samples of varying thickness. Clearly this is a point where the previously mentioned scattering techniques have advantages in quantization.

In summary, the TEM sample must be thin enough to avoid excessive overlap pores through the projected section, but it should not be much thinner than the average pore diameter to be measured. Thus to interpret pore distribution data the sample thickness should be known.

**DETERMINATION OF TEM SAMPLE THICKNESS**

TEM sample thickness may be determined by electron energy loss spectrometry (EELS) using the EELS log-ratio method\textsuperscript{10} (facilitated in the most commonly used EELS software). However, this only works for materials where the inelastic mean free path (\(\lambda\)) is known or calculable. For porous low-k, \(\lambda\) cannot be determined because of the density fluctuations due to the random distribution of pores.

For imaging pores with diameters of a few to a few tens of nanometers, TEM samples need to be of thickness not greater than 100 nm. This is too thin for accurate thickness determinations by CBED, but is fine for EELS methods.

\[
\text{thickness} = \frac{T}{\sin \beta}
\]

Figure 7. Use of carbon contamination spots deposited with a focused electron probe (as in STEM) by imaging at two tilts to determine thickness from image parallax.

Figure 8. HAADF-STEM images of a cross-section through a porous low-capped with platinum (bright contrast) and TEOS capping layers. Carbon contamination was deposited on the TEOS with the sample at a beta-tilt of zero, and the separation between spots on top and bottom of the sample were measured at a tilt of 10 degrees to allow a thickness calculation. Parallax is also observed in measurement of the thickness of the platinum coating.

A common and often maligned method of determining sample thickness involves imaging of contamination spots that form when the electron probe is focused and held stationary on the sample. Contamination spots form at both surfaces of the sample as the electron beam cracks mobile surface hydrocarbons that tend to contaminate the surface. Figures 7 and 8 show the geometry and data used to determine sample thickness from tilt-views of contamination spots. This method has been criticized for inaccuracy, however it seems that with modern FEG instruments significantly smaller probes can allow the deposition of very small contamination spots and we have seen results that match well with EELS measurements. Contamination spots do not deposit well on low-k as the porosity leaves a question of...
whether the deposition is on the surface or inside the pores within the thickness of the TEM sample. Figure 8 shows that tilting the sample also creates a parallax in the view of structures in the sample that can similarly be used for determining the sample thickness. In either case, differences in ion milling rates must be considered in interpreting the sample thickness.

As discussed previously, a porous dielectric may ion-mill faster than more dense materials like the silicon substrate. Still, measurements of the adjacent material thickness can at least provide an upper bound for porous low-k thickness.

QUANTITATIVE MEASUREMENTS OF PORE SIZE AND DENSITY DISTRIBUTIONS

Measurements can be made by hand following a lineal intercept method over a known area like that delineated by the box drawn over Figure 9. The volume represented by this box can be determined once the sample thickness is known, and if the pore volume is calculated (facilitated by assuming that pores have simple geometric shapes), then a percent porosity can also be calculated.

![Figure 9. Conventional TEM image from a very thin region of a blanket low-k film showing small (approximately 2.9 nm average diameter) pores. The red box (175 nm x 25 nm) shows the region from which pore diameters were measured.](image)

The pore size distribution data, plotted as shown below in Figure 10, compared well with PALS data from the same sample showing an average pore size of 2.92 +/- 0.08 nm. However, similar data for low-k films with average pore sizes less than 2.5 nm did not match as well; this may represent the limit of the TEM capability and is likely related to limits in our ability to prepare TEM samples thinner than a few tens of nanometers.

![Figure 10. Size distribution plotted for pores measured from the red-box region of the TEM image shown in Figure 10.](image)

Automated image analysis is difficult using conventional TEM images as amorphous films show "speckle" contrast resulting from the complex contrast inversions that oscillate as a function of frequency. Smoothing the speckle in such images without losing the contrast required to observe pore structure can be difficult.

HAADF-STEM images are better suited to software-based image analysis routines because this technique has a simpler contrast dependence more linearly related to the average atomic number (Z-contrast) of material through which the focused probe must pass (Fig. 11a). Smoothing to reduce pixel-to-pixel statistical noise and background flattening

![Figure 11. (a) Raw HAADF-STEM data (b) background flattened (c) thresholding was set manually to delineate pores (d) image analysis result after pores defined by threshold setting and minimum size to avoid noise pixels.](image)
(Fig. 11b) are necessary to produce data suitable to image analysis. Thresholding (Fig. 11c) allows segmentation of an image based on a particular gray-scale level. The image analysis was performed using Lispix software.\textsuperscript{11} From the segmented data, image analysis software can quantify pore sizes and numbers that can be used with sample thickness to determine density distributions. However, thresholding relies on a subjective choice of gray-scale level that may vary depending on sample thickness, material density and microscope parameters. The annular dark-field detector bias and gain settings need to be selected to maximize the number of gray-scale levels in the image relating to pores; contrast relating to other features in the image (like the platinum coating seen in Figure 9) can be set off-scale to improve contrast levels in the low-k.

**SUMMARY**

Distributions of pores in low-k films can be well characterized by TEM. In particular TEM is good for showing changes in pore distribution as a function of depth into a film or near device structures related to processing. Sample preparation must be conducted with care to avoid pore filling or damage. The thickness of the TEM sample affects the ability to observe pores, and this thickness must be known to allow quantitative analysis of pore distributions. For the thin TEM samples required for pore imaging, sample thickness is best determined by EELS from dense material with known properties such as silicon or SiO\textsubscript{2}, or by geometric analysis from tilted images showing structures that run through the sample thickness. Contrast in conventional TEM images can be enhanced to show pores by defocus to Fresnel conditions, but HAADF-STEM provides images with better contrast behavior for software-based image analysis. TEM may be limited in ability to measure pores less than a few nanometers in diameter primarily because of limits to the stability of TEM samples thinner than a few tens of nanometers.

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