TEM sample preparation by FIB for carbon nanotube interconnects

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1. Introduction

Interconnects play a key role in integrated circuits (ICs). Copper interconnects are now being routinely used with minimum feature sizes down to 45 nm [1]. However, the electrical resistivity of Cu increases with decrease in dimensions due to electron surface scattering and grain boundary scattering, which is difficult to overcome [2,3]. Alternatives are therefore necessary and carbon nanotubes (CNTs) are considered as a potential solution [3–5]. Calculations have shown that CNTs can potentially outperform copper in contact holes [6,7]. Previous work of growing CNTs in contact holes has been carried out [5,8,9], but its development and integration processes are challenging and require the ability to locally characterize CNTs. Recently a pick-and-place method is reported for transfer of individual CNTs from a contact hole to a copper grid with the assistance of a nanomanipulator in a scanning electron microscope (SEM) for further study [10]. An earlier study also succeeded in showing cross-section images of CNTs in one contact hole [11]. Obviously, detailed knowledge is required on how the CNTs are grown in situ, how catalysts perform during the growth of CNTs and how the contact is formed and is related to the substrate.

A powerful method to acquire such information is transmission electron microscopy (TEM). However, high-quality TEM samples are necessary for such a study. Here, TEM specimen preparation by focused ion beam (FIB) has been used to obtain lamellae of patterned samples containing CNTs inside contact holes. A dual-cap Pt protection layer and an extensive 5 kV cleaning procedure are applied in order to preserve the CNTs and avoid deterioration during milling.

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thicknesses of 70 and 30 nm, respectively, are deposited for contact reasons. Then, amorphous SiO$_2$ with nominal thickness of 300 nm is deposited, in which arrays of so-called “contact holes” are etched. The test structures consist of arrays of contact holes with nominal diameters of 130–300 nm. CNTs are then grown inside the contact holes after catalyst particles have been electrodeposited inside [9,15]. Bundles of CNTs or single CNTs may grow in the contact holes, as illustrated in Fig. 1. In order to avoid the difficulty of imaging overlapping CNTs, as may happen in the case of a high density of CNTs grown in one contact hole, 130 nm contact holes containing a single CNT are investigated in the present study (Fig. 1c).

FIB sample preparation is performed using a FEI Nova 200 Nanolab DualBeam SEM/FIB system. A standard ion column is installed, which allows Ga milling at 5–30 kV. The ion column axis is positioned under an angle of 52° with respect to the electron column axis. The system is also equipped with an in situ gas injection system loaded with a Pt deposition needle and an OMNIPROBE$^{TM}$ extraction needle.

High resolution TEM (HRTEM) and energy filtered TEM (EFTEM) are performed on a CM30 FEG microscope, operated at 300 kV, which is equipped with a GIF200 post column energy filter: high-angle annular dark field scanning TEM (HAADF-STEM) measurements are carried out on a JEOL3000F operated at 300 kV.

3. FIB sample preparation

Electron microscopy samples are prepared by standard FIB preparation following the basic principles of this technique documented before [16,17] but with a few modifications.

Deposition of a protective Pt layer is always applied to the area of interest prior to milling. In general, the Pt protection layer is deposited using ion beam induced deposition (IBID). This has the advantage of depositing a thick protection layer within a short time. The as-deposited protection layer is not pure Pt but contains a considerable amount of C and Ga, of which the exact composition may vary depending on deposition parameters [18]. Unfortunately, the IBID Pt layer can damage the surface of the region of interest because of the energetic Ga$^+$ ions used during this procedure. In fact, the ion beam is not only inducing Pt deposition but also milling away or amorphizing the sample surface. The typical depth of damage caused by IBID is about 100–200 nm [19]. In the present study, CNTs may grow out of the contact holes and are therefore exposed to IBID damage. One solution is to perform the deposition of the protective layer in two steps: first electron beam induced deposition (EBID) followed by IBID [18,20]. EBID deposition requires a quite high electron dose so that electron beam-sensitive materials might be damaged. However, due to the low beam energy these effects can be expected to be less important. Although it has been reported that EBID can still induce damage to the surface, the depth of amorphization damage is dramatically reduced to 10–20 nm [21]. The deposition steps are illustrated in Fig. 2. An area of interest is selected as shown in Fig. 2a. The first deposition process consists of EBID Pt, approximately 1.2 μm wide by 8 μm long with a total nominal deposition thickness of 300 nm (Fig. 2b). An incident electron beam energy of 18 kV and a beam current of 0.6 nA is applied to perform the deposition. It results in an acceptable compromise between Pt content and deposition rate as the atomic Pt content in EBID decreases as a function of the beam energy whereas the vertical growth rate increases by the decrease of beam energy and increase of beam current [22,23]. Then, an IBID Pt of the same size is applied on top of the EBID Pt with an additional thickness of 1 μm (Fig. 2c). In this manner, a dual-cap protection layer is formed to protect the CNTs from ion beam damage during subsequent milling.

![Fig. 1.](image)

(a) Illustration of contact holes; (b) SEM image of a certain area from the specimen’s surface; (c) enlargement of the boxed area in (b) shows that one single CNT can grow in each contact hole.
Next, a staircase thinning at 3 nA at both sides of the region of interest is performed until a lamella with a thickness of approximately 1 μm is obtained. Directly after this step the specimen is tilted over 7° with respect to the ion beam and an undercut is made to release the sample by a needle. Next, the specimen is welded to the needle and lifted out of the substrate; the stage is then moved to a different holder that contains a TEM grid onto which the specimen is welded. The TEM grid used in this study is Omniprobe® GRD-0001.01.01 Cu Lift-out Grid. After the sample is attached using in situ Pt deposition, the needle is separated from the specimen.

In the following step, the specimen is thinned from both sides gradually using a 30 kV ion beam and a current of 30 pA. Since the specimen contains contact holes approximately in the middle of the lamella, a different contrast is present when the milling approaches the contact holes. Fig. 3a shows this contrast when imaging using SEM. This contrast indicates that thinning at 30 kV should be stopped to prevent damage and the formation of an amorphous layer onto the contact holes. Next, the stage is rotated over 180° and the same thinning procedure is repeated to the other side of specimen until the contrast of contact holes shows up. In practice, this last milling step can be carried out by small steps using a “cleaning cross-section” pattern. A cleaning cross-section pattern approaches the area of interest line by line, which minimizes redeposition effects onto the sample sidewalls [24]. This process is monitored by live SEM imaging.

Using FIB, a specimen thickness of approximately 100 nm is often the final goal, but this rule does not apply to our particular samples. The final thickness of the specimen depends on the size of the contact holes to be investigated. For instance, the contact holes selected in this study have a nominal diameter of 130 nm. Therefore, when the thinning procedure as described above is completed, the specimen is estimated to have a thickness of about 150 nm or even more. Nevertheless, TEM requires electron-transparent specimens of approximately 100 nm thick. HRTEM and other advanced TEM studies require even higher quality lamella with a thickness of approximately 50 nm. Therefore, an additional low kV thinning procedure is required to prepare a fine lamella suitable for advanced TEM studies.

Low kV thinning is carried out at 5 kV with a small current on both sides of the specimen. First, a current of 29 pA is used to thin the specimen down to about 90 nm, which can be monitored by the SEM. A SEM image after this step of fine milling is shown in Fig. 3b. During this process the stage is tilted 1.2° positive and negative with respect to the incident ion beam in order to prepare parallel sidewalls. The angle required depends on the ion–solid interaction with the specimen. For slower sputtering materials such as CNTs and a matrix of amorphous SiO2, a 1.2° incidence angle is often used [24]. Finally, thinning and cleaning are carried out at 10 pA. This step needs to be carried out with care by repeating approximately 1 min milling for 3–5 times from both sides by using a cleaning cross-section. During this step, the dual-cap Pt protection layer starts to be milled away and an electron-transparent lamella is made. This process needs to be closely monitored by live SEM imaging.

### 4. Dual-cap investigation before the low kV cleaning

First, the effect of using a dual-cap protection layer will be investigated. The as-prepared specimens are studied by SEM as shown in Fig. 4. The contact hole, as measured on the image, has a diameter of about 110 nm, whereas its nominal size is 130 nm. This
indicates that the lamella is cut close to the middle of the contact hole. In Fig. 4a, the specimen is prepared using only IBID Pt, whereas Fig. 4b and c present similar specimens where dual-cap protection layers are applied. For lamellae shown in Fig. 4b and c, the CNTs growing above the holes are protected better compared to the case in Fig. 4a. The dual-cap protection layers hardly alter either the size or the shape of the covered CNTs. This clearly illustrates the advantage of using a dual-cap protection layer.

The dual-cap protection layer of the lamella shown in Fig. 4b is then studied by conventional TEM and HAADF-STEM. In Fig. 5 a bright field (BF) TEM image and a HAADF-STEM image of the same region are compared. The W contact layer and the SiO2 matrix where contact holes are etched can be distinguished thanks to the chemical sensitivity of HAADF-STEM, which is strongly dependent on the atomic number Z. Note that at the bottom of the contact hole the contrast of the catalysts is still present, as indicated by the arrow. The CNT is growing out of the catalytic material and up through the contact hole. The tip of the CNT, present above the hole, is well embedded in the dual-cap protection layer, as the SEM study also indicated. It is not obvious to see the contrast of the CNT in this case, since C yields a low contrast in TEM. EFTEM is performed with the carbon map shown as the inset in Fig. 5. The carbon map shows the CNT tip, which has a strong carbon signal. In addition, a certain intensity of carbon signal is present around the CNT tip as well. This signal is due to the EBID Pt, which consists of more than 70% of carbon and less than 30% of Pt. EBID is a process by which a solid material is deposited onto a solid substrate by means of an electron-mediated decomposition of a precursor molecule [25], which is (CH3)3Pt(CpCH3) in the present study. As the electron beam is only accelerated to 30 kV, the decomposition of the precursor is far from complete. Therefore EBID often produces Pt nanoclusters embedded in amorphous matrix of carbon. Using IBID, the decomposition of the precursor molecule is performed by ions, which is more efficient since the ions carry more energy. Therefore the IBID Pt contains less C. Note however that the IBID Pt layer may contain an amount of Ga induced by the ion beam. This fact also leads to a brighter contrast of IBID Pt and a darker contrast of EBID Pt in the dual-cap layer as presented in the HAADF-STEM image and vice versa in the BF-TEM image.

5. CNT investigation after low kV cleaning

A final milling/cleaning step was carried out as described in the sample preparation section. During this step, the FIB milling should be carried out carefully after the IBID Pt is milled away and only the EBID Pt of the dual-cap protection layer is present. The remains of the EBID Pt layer can be removed quite easily and therefore the CNT may be completely exposed to the ion beam. The main reason is that the tail of the 5 kV ion beam results in much more rounding at the top edge of the lamella. A detailed discussion of this enhanced rounding effect at low kV cleaning is treated in the discussion section. The lamella at this step is presented in Fig. 4c, which has a thickness of only 40–60 nm and therefore is suitable for HRTEM investigation.

Fig. 6a presents a cross-section HRTEM image of the contact holes. Embedded in an amorphous matrix, shells on both sides can be distinguished, as indicated by red lines. Enlargements of these shells from both sides are shown in Fig. 6b and c. The intensity profile through the shells is shown in Fig. 6d; from this profile the inter-distance between shells is measured to be 0.34 nm, which is the distance expected for MWCNT walls. These experiments clearly illustrate that the inner shell structure of the CNT is preserved during the FIB preparation process.

Apart from the symmetric shells found at both sides of the hollow core, a few pieces of discontinuous CNT walls are found to be present as well, as indicated by yellow arcs in Fig. 6a. The presence of these curled shells has several possible origins. It is possible that they are artifacts/defects of the CNTs, which are commonly observed in CVD-grown CNTs. It is also possible that they are caused by FIB milling. When a CNT grows inside a contact hole, it may not fill up the entire space in the hole. For the contact holes with a nominal diameter of 130 nm, most as-grown CNTs have a diameter of 40–60 nm, as measured by SEM. In addition, the CNTs may not grow strictly vertical along the contact hole but wind their way through. Therefore, it is virtually impossible to have the lamella with the CNT in the centre over the full length of the CNT. Therefore parts of the CNT can be milled away and only pieces of the CNT are preserved, as illustrated in Fig. 7 for several possible situations. The different cases are difficult to distinguish as the TEM image is a 2D projection over the thickness of the TEM lamellae. Electron tomography could be a solution to overcome this problem [26].

In Figs. 6 and 7, small areas of dark contrast are visible on all HRTEM images. The contrast is attributed to small clusters of Pt metal; this has been confirmed by EDX. The presence of Pt around the CNTs inside the contact hole is mainly due to the deposition of EBID Pt. This is difficult to avoid, as the CNTs do not fill up the entire space in the contact holes and therefore the contact holes are not fully covered by the CNTs (see Fig. 1c), part of the EBID Pt fills in the space inside the contact holes.
Fig. 5. BF and HAADF-STEM study of the same contact hole where the as-grown CNT is covered by dual-cap protection layer. The carbon map shown as inset provides the distribution of carbon element at the CNT tip.

Fig. 6. Presents HRTEM study of the CNT preserved in contact holes in situ. The HRTEM image is shown as (a). The enlargements of the CNT shells are presented as (b) and (c). An intensity profile through the CNT shells is shown as (d).
6. Discussion

It has already been shown in the past that FIB is an excellent technique to prepare TEM samples, especially in the field of semiconductor research and industry. Here, a modified approach is proposed to prepare samples of CNT interconnects with the structure of CNTs grown in contact holes.

6.1. Dual-cap layer

A dual-cap protection layer is used to protect the CNTs from destruction by ion milling. The idea of a dual-cap layer has been mentioned in earlier studies [18,20], and we have demonstrated how important this method is to protect the delicate surface features like CNTs. When only IBID Pt is used, the sticking out parts of the CNTs are undoubtedly destroyed and the contact hole will also be inevitably filled. The IBID Pt contains more amount of Pt than the EBID Pt and the high contrast of this heavy metal Pt will certainly make the CNTs invisible in (S)TEM. Therefore the use of a dual-cap layer is very important.

During the last steps of 5 kV cleaning, the remains of the dual-cap Pt layer can be removed quite easily, as mentioned before. On the one hand, as the accelerating voltage of the ion beam decreases, the beam is less focused, and therefore the spot size of the ion beam increases. When the current of 29 pA is applied during the 5 kV thinning procedure, the spot size is 61.2 nm; when the current of 10 pA is applied during the last step of the 5 kV thinning, the spot size is 46 nm. On the contrary, when a current of 30 and 10 pA is applied for a 30 kV ion beam, the spot size of the beam is only 16 and 12 nm. Obviously, the low kV cleaning causes a broader and less-focused ion beam. One should also realise that the incident FIB spot not only has a fixed size but also presents an approximately Gaussian distribution of intensity [27]. Moreover, an additional exponential tail of the beam has also been reported [28]. Therefore, when a FIB spot is scanned to mill the specimen, the side wall has a certain slope. As a consequence the FIB milling cross-sections are not perfectly parallel to the beam but result in a top rounded tapered shape, reported both experimentally and theoretically [27]. Although we tilted the sample away from the axis parallel to the incident beam, a rounding near the top edge cannot be avoided in the cross-section specimen. This is due to unwanted sputtering by the tails of the FIB spot, especially in the last 5 kV cleaning where the spot size is already broad and rounding effect can be worse. Since during this last step of FIB preparation the specimen is already thin, the enhanced rounding effect during FIB milling at both sides of the lamella results in the removal of IBID as well as EBID Pt layer, which may leave the CNT completely exposed to the ion beam. Therefore, the protection layer has to be deposited thick enough in the first place.

6.2. Preservation of CNTs in situ in the SiO2 matrix

A Ga⁺ beam is generally used to mill metal or semiconductor materials, which are harder materials compared to CNTs. CNTs are not only soft material but also quite beam-sensitive under the exposure to either ions or electrons. Nevertheless, we have successfully shown that the CNTs can be preserved from complete amorphisation, although a slight modification and destruction of the CNTs is inevitable. Furthermore, we have succeeded in preserving the soft CNTs in situ within a matrix of SiO₂, which is the harder material.

Milling was carried out with a 5 kV ion beam, which is the lower limit of the instrument. Recently, ultra-low kV FIB milling became commercially available, e.g. 2 kV and even 1 kV in the latest instruments. Since it has been successfully shown here that 5 kV milling can preserve the CNTs in situ in the contact holes, lower energy FIB milling will certainly result in even higher quality TEM samples.

In order to obtain a better cleaning of the sample, a post-treatment was carried out. Ar⁺ ion beam milling was performed ex-situ at a voltage of 0.8 kV for 20 min at a small angle. However, the sample did not show any obvious improvement. Plasma cleaning is usually applied to clean the specimen surface before TEM investigation. Nevertheless, in the general study of the CNTs, plasma treatment is seldom applied as it may alter the as-grown structure.

Fig. 7. (a) Shows that only one side of the CNT shells is found from the contact hole of an as-prepared lamella. (b) Presents a lamella containing pieces of CNTs.
6.3. Limits of the technique and prospects

Although samples have been successfully prepared for qualitative HRTEM work, there are certain limits for this preparation technique. First, it should be realised that the CNTs can be modified by the energetic Ga+ ions. Despite the fact that a 5 kV ion beam is applied to minimize the amorphous layers on the sample and to preserve the CNT structure as good as possible, the energy carried by Ga+ ions undoubtedly exceeds the theoretically calculated knock-out energy of carbon atoms in CNTs. Therefore, destruction of the outer shells of the CNTs is virtually impossible to avoid. Moreover, a slight amount of Ga+ ion may have been implanted into the sample, which is common to all FIB prepared lamella.

As the CNT does not grow strictly vertical in the contact hole, it is virtually impossible to have the lamella with the CNT in the centre over the full length of the CNT. Therefore, it is difficult to guarantee that each lamella will have the cross-section of an entire CNT. In Fig. 7a, e.g., only part of the CNT is present.

Also, the EBID Pt filling inside the contact hole during protection layer deposition hampers the interpretation of the CNTs. As it is inevitable that the EBID Pt fills up the space in the contact hole, the Pt nanoclusters coat the outer shell of the CNT, however without damaging the CNT.

Regarding the application of CNTs in contact holes as future interconnects, it has now been shown that the FIB sample preparation is able to preserve the CNTs in the contact holes, and further investigations can be carried out including not only low-density CNTs but also high-density CNTs grown in situ in contact holes. A high-density of CNTs in a contact hole will complicate CNT density CNTs but also high-density CNTs grown in situ in contact holes. Further investigations can be carried out including not only low-density CNTs but also high-density CNTs grown in situ in contact holes.

7. Conclusions

FIB specimen preparation using a dual-cap Pt protection layer and extensive low kV (5 kV) cleaning has been applied to prepare TEM samples from contact holes containing single CNTs. By SEM, HRTEM, HAADF-STEM, and EFTEM it has been demonstrated that the milling and cleaning process yields samples in which the CNTs inside contact holes have been preserved. The success of preparing such specimens for low densities of CNTs in the contact holes has opened ways for further application to high densities of CNTs.

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