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Fabrication of Carbon Nanotube Via Interconnects at Low Temperature and Their Robustness over a High-Density Current

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We fabricated carbon nanotube (CNT) via interconnects (vertical wiring) and evaluated their robustness over a high-density current. Multiwalled carbon nanotubes (MWNTs) were grown at temperatures as low as 365°C using Co catalyst nanoparticles, which were formed and deposited by a custom-designed particle generation and deposition system. MWNTs were successfully grown in via holes with a diameter as small as 40 nm. The resistance of CNT vias with a diameter of 160 nm was found to be of the same order as that of tungsten plugs. The CNT vias were able to sustain a current density as high as 5.0×10^{6} A/cm^2 at 105°C for 100 h without any deterioration in their properties.

1. Introduction

Advanced large-scale integrated circuits (LSIs) employ copper (Cu) as an interconnect material because of its low resistivity. The continuing shrinkage in the dimensions of LSIs, however, increases the current density in the Cu interconnect, which makes the Cu interconnect unreliable owing to electromigration problems. Carbon nanotubes (CNTs) are one of the most promising candidates to replace Cu as an interconnect material owing to their excellent electrical properties. These include abilities to sustain a current density as high as 10^{9} A/cm^2,[(1)] which is two to three orders of magnitude higher than that for Cu, and to exhibit a ballistic transport along the tube.[(2)]

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In fact, there have been several reports on the use of multiwalled carbon nanotubes (MWNTs) for LSI via interconnects (vertical wiring).[3–6]

To construct CNT vias, however, there are several issues to be addressed. One of them is the need to lower the electric resistance of the CNT vias. Apparently, the higher the number of CNTs in a via hole, the lower the resistance. Although closely packed CNTs are desirable, it is not easy to grow such CNTs. We previously grew MWNTs in via holes using a sputtered Co film as a catalyst, and the site density of the MWNTs was around 5×10^{10} cm^{-2}, which accounted for only a few percent of the space in the via hole.[7] In such a case, it is believed that the Co film separated into particles by heating and that MWNTs grew from such particles. To increase the CNT density further, the number of particles in the via hole should be controlled. Another issue is to lower the growth temperature of CNTs. A growth temperature of 450°C or lower is a minimum requirement to avoid any damage to LSIs. In our previous studies above, the growth temperature ranged from 540 to 450°C.[3,4,7] Although studies regarding low-temperature CNT growth have been reported,[8–10] there are few studies showing the electrical properties, especially maximum current density, of CNTs grown at low temperatures down to 400°C. One of the other important steps for realizing CNT vias is to develop a fabrication process that is compatible with standard LSI processes. In particular, the planarization of a substrate with CNT vias is essential.

In this paper, we introduce our recent progress in developing CNT via technologies.[12–14] We first describe a novel process for fabricating CNT vias. This process includes the deposition of size-controlled catalyst nanoparticles using a custom-designed particle deposition system,[11] the low-temperature growth of MWNTs (510–365°C) using such catalyst particles,[12,13] and the planarization of a substrate with CNT vias by chemical-mechanical polishing (CMP).[14] We then show the electrical properties of vias made of bundles of MWNTs, including their electrical resistance and robustness over a high-density current.[12,13]

2. Materials and Methods

2.1 *CNT via process*

A typical fabrication process for a CNT via is schematically shown in Fig. 1. A substrate with a Cu interconnect covered by a dielectric layer was first prepared. The dielectric layer was SiOC with a dielectric constant (k) of 3.0 or 2.6. Via holes with a diameter of 160 nm were made using conventional photolithography followed by dry etching. A TaN/Ta barrier layer and a TiN contact layer were deposited by physical vapor deposition (PVD). Size-controlled Co particles with a mean diameter of about 4 nm were then deposited using a custom-designed particle generation and deposition system, whish is explained in the following subsection. MWNTs were grown by thermal CVD with C_2H_2 diluted by Ar as the source gas. The pressure of the source gas was 1 kPa. The substrate temperature ranged from 365 to 510°C. The substrate with MWNTs was then coated with spin-on glass (SOG) and planarized by CMP. The CMP condition was similar to that used for polishing a silicon dioxide layer. The substrate was polished

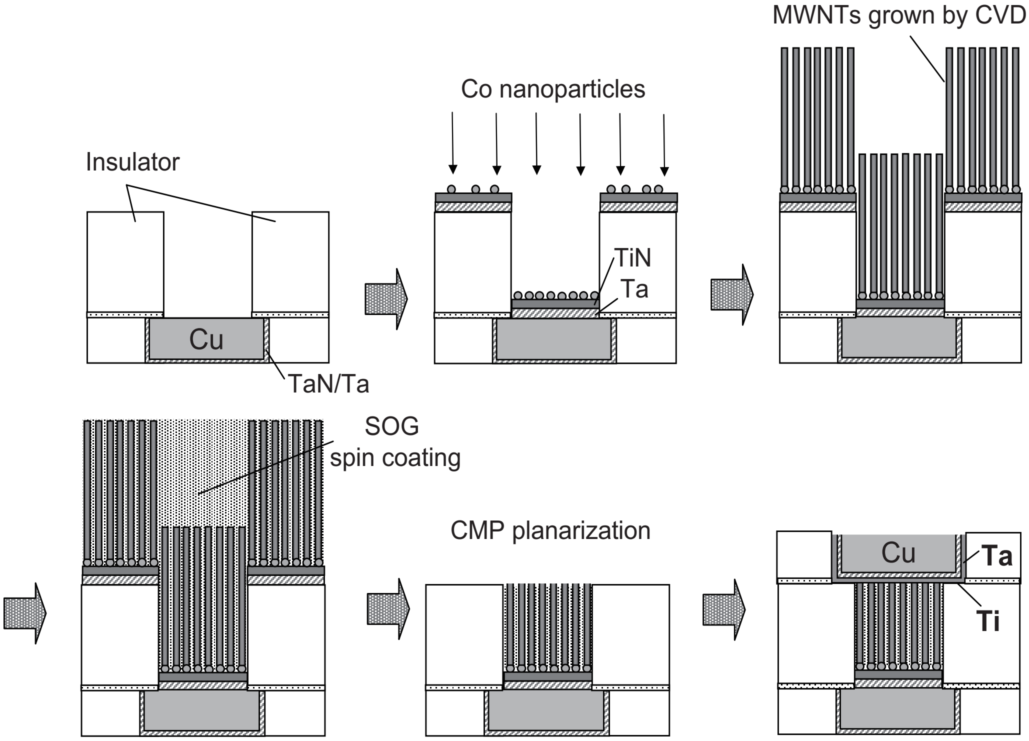


Fig. 1. Typical fabrication process for a CNT via.

with a conventional IC1000 pad and silica slurry under a pressure of 2 psi (13.8 kPa) for 150 s. Finally, a Ti top contact layer, a Ta barrier layer, and a Cu wire were connected to the CNT vias by PVD. Although CNT vias with a diameter of 160 nm were mainly used for evaluating the electrical properties, we also prepared CNT vias with different diameters, ranging from 2,800 to 40 nm.

2.2 *Preparation and deposition of catalyst nanoparticles*

In this subsection, the particle generation and deposition system used in this study is described. This new system was briefly described in our previous paper,(15) but a more detailed description is given here. The system is schematically illustrated in Fig. 2. Cobalt catalyst particles were generated by the laser ablation of a Co target in a low-pressure He environment (~1 kPa).(16,17) A pulsed Nd:YAG laser (wavelength: 532 nm; power: 2 W; repetition frequency: 20 Hz) was employed for this purpose. The particles were then brought to a size classifier consisting of an impactor with a 1-2 slpm flow (standard liter per minute) of He carrier gas. An impactor is a piece of apparatus often used in the aerosol field in order to collect ambient particles using their inertia.(18) Here, we designed

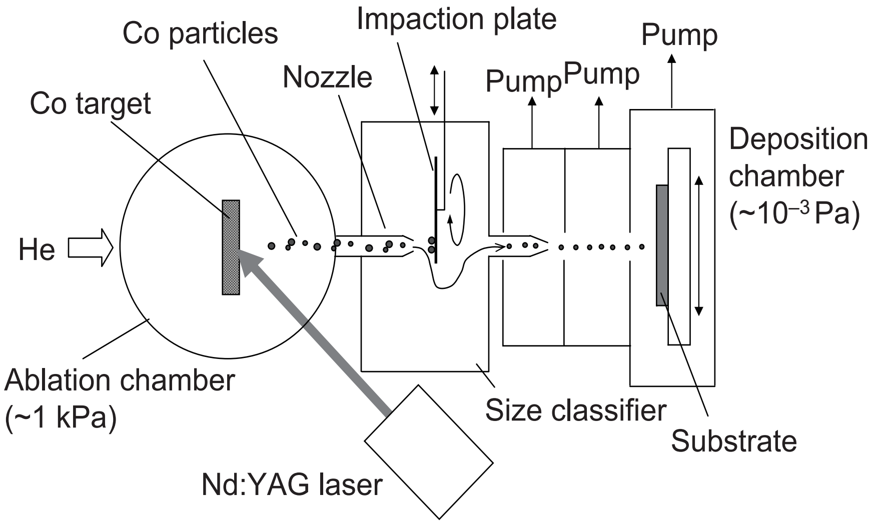


Fig. 2. Particle generation and deposition system.

an impactor for classifying particles smaller than 5 nm, which has probably not yet been attempted. Briefly, an impactor consists of a nozzle and a downstream impaction plate. Particles are accelerated with a carrier gas in a nozzle and directed to the impaction plate. If the inertia of the particles is sufficiently large, they collide with the plate and are collected. As a result, the particles with a small inertia (i.e., small particles) are transported downstream with the carrier gas. The size of particles penetrating with a 50% probability (cut size) can be controlled by certain parameters, such as gas flow rate, gas pressure, and nozzle diameter.(18) Although the impactor removes only large particles, nanometer-size particles typically have a smaller size limit due to particle growth by condensation and coagulation. Therefore, particles with a relatively narrow size distribution can be obtained only by using the impactor. In our experiments, the experimental conditions were optimized to obtain particles with a mean diameter of ~4 nm. The size-classified particles were then brought to a high-vacuum deposition chamber (~10^{-3} Pa) utilizing differential pumping to produce a directed particle beam. The directed particles were deposited onto a substrate with via hole patterns. The movable substrate stage enabled particle deposition all over the substrate. The current system can handle a substrate up to 200 mm in diameter. The typical deposition rate was 10^{13}–10^{14} min^{-1}, which was about 1,000 times higher than that of the previous system using the differential mobility analyzer (DMA).(16,17) We expect that the deposition rate will be increased further by scaling up the system.

3. Results and Discussion

3.1 *Nanoparticles classified with the impactor and performance of the deposition system*

A scanning electron microscopy (SEM) image of Co particles classified with the impactor is shown in Fig. 3(a). A transmission electron microscopy (TEM) image along with an electron diffraction pattern is also shown (Figs. 3(b) and 3(c), respectively). In this case, the Stokes number, which is a dimensionless parameter for controlling particle deposition in an impactor,[18] was 0.5 for particles with a diameter of 4.2 nm.

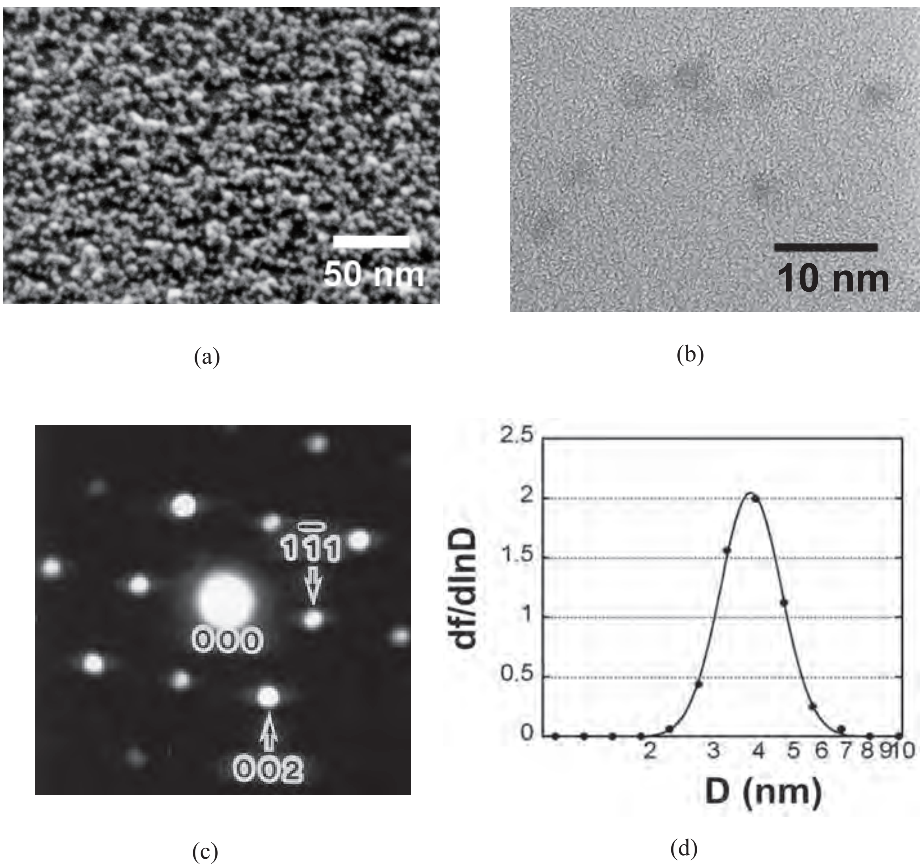


Fig. 3. Cobalt particles obtained using the particle generation and deposition system: (a) SEM image; (b) TEM image; (c) electron diffraction pattern from a Co particle; and (d) size distribution obtained from TEM images. The vertical axis shows a number fraction divided by the logarithmic range width. The curves were obtained by fitting a log-normal distribution to the distribution data.

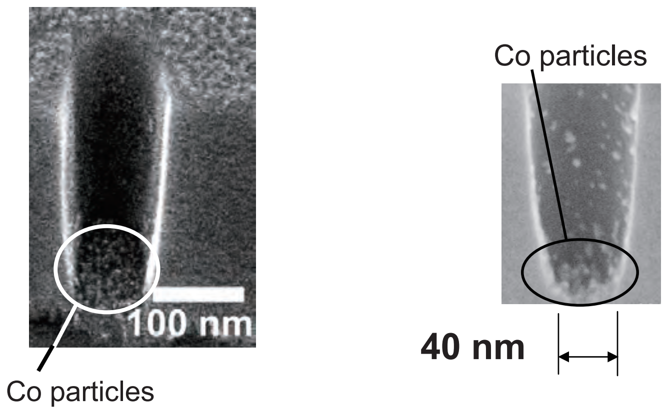
The geometric mean diameter and geometric standard deviation obtained from the TEM images were 3.8 nm and 1.21 (meaning ~21% deviation), respectively (Fig. 3(d)).

Figure 4(a) shows cross-sectional SEM images of test via holes with a lateral size of ~100 nm after particle deposition. Particles at the bottom of a via hole can be clearly seen, while there are few particles found on the sidewall. The particles were also deposited at the bottom of a 40-nm-diameter hole (Fig. 4(b)).

In our deposition system, the directionality of particles can be controlled according to the choice of orifices used in the differential pumping unit. Therefore, in principle, our system can deposit catalyst particles at the bottom of via holes with an even smaller diameter and a higher aspect ratio.

3.2 *CNTs grown in via holes*

Figures 5(a) and 5(b) show cross-sectional SEM images of MWNTs grown in via holes with a diameter of 160 nm at growth temperatures of 450 and 400°C, respectively. We can see in the images that MWNTs grown at 400°C are slightly less straight than those grown at 450°C, suggesting that MWNTs at 400°C are slightly more defective. To elucidate the quality of MWNTs, we performed TEM analyses, and the results are shown in Figs. 6(a) and 6(b). The TEM images indicate that MWNTs grown at either temperature are of high quality, although, again, MWNTs at 400°C might be slightly more defective. Incidentally, it is considered that the low-temperature growth we have achieved is partly due to the existence of the TiN layer under Co particles. In fact, we could not grow CNTs under the same growth conditions without the TiN layer. This result is similar to our previous experimental results showing that alloy particles



(a) (b)

Fig. 4. Cobalt particles deposited in via holes with (a) a lateral size of 100 nm and (b) a diameter of 40 nm.

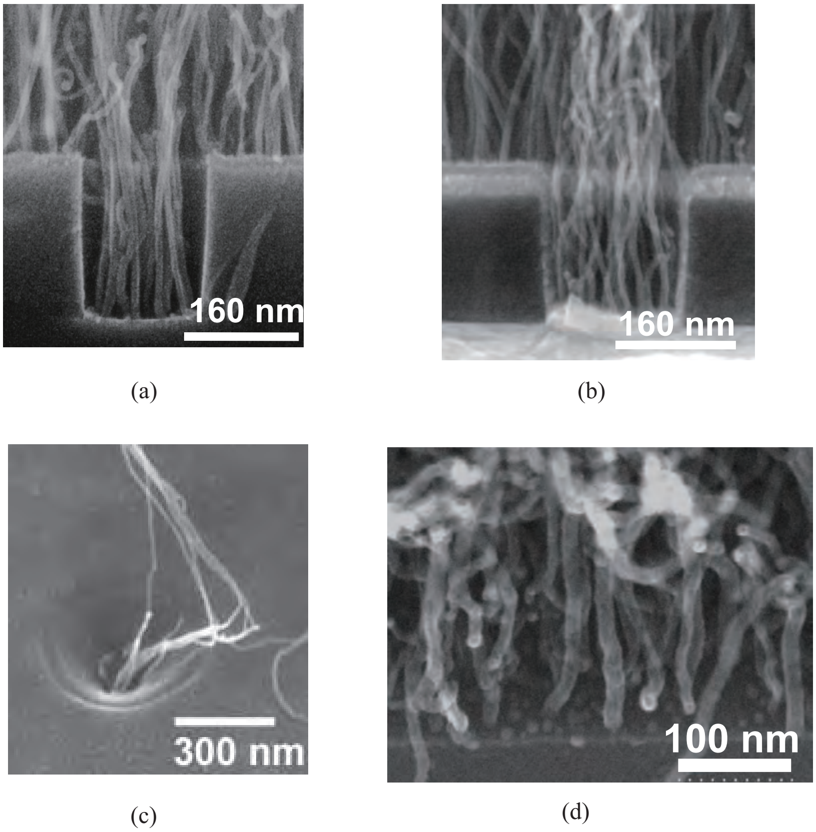
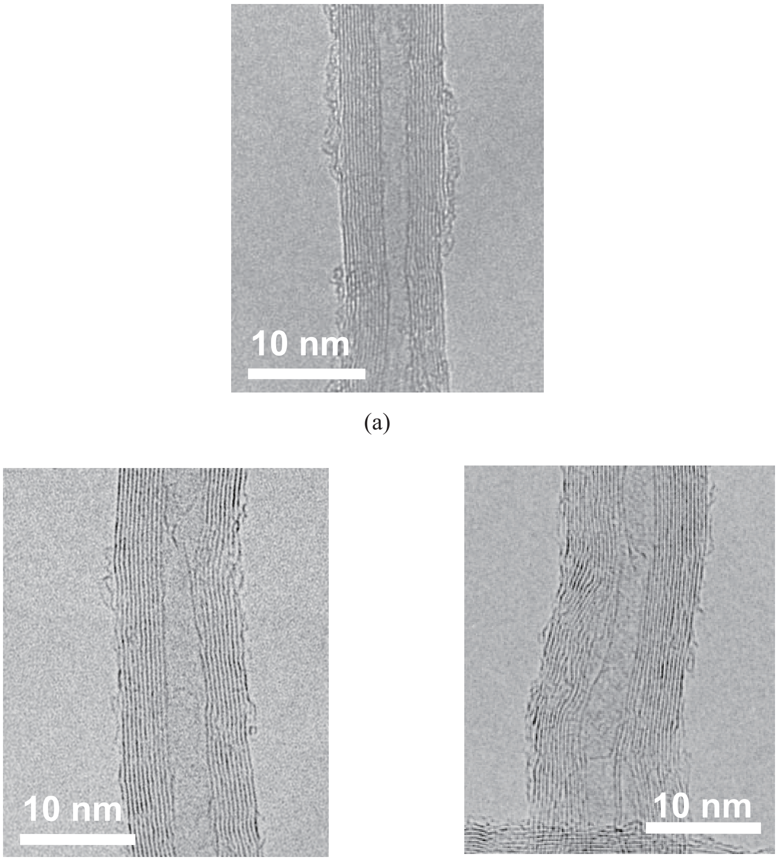


Fig. 5. Cross-sectional SEM images of MWNTs grown in a via hole at (a) 450 and (b) 400°C. (c) SEM images of MWNTs grown in a via hole with a diameter of 40 nm at 510°C. (d) SEM image of MWNTs grown at 365°C.

consisting of Co and Ti are a more effective catalyst for CNT growth than pure Co particles.(17)

The average site density of MWNTs in the 160 nm via holes was 3×10^{11} cm^{-2}. Figure 6(c) shows MWNTs grown in a via hole with a diameter of 40 nm (growth temperature: 510°C). In this case, the MWNT density was 9×10^{11} cm^{-2}. The site densities of MWNTs were higher than those in the previous studies in which a catalyst film was used for CNT growth.(3,4,7) However, the particle site density was actually about 5×10^{12} cm^{-2}; thus, we have not yet succeeded in growing MWNTs from all the particles available.

Incidentally, Figs. 5(d) and 6(c) respectively show the SEM and TEM micrographs of MWNTs grown at 365°C. Surprisingly, the product still has a tubular structure. We plan to fabricate vias made of MWNTs grown at this low temperature in the near future.



(a)

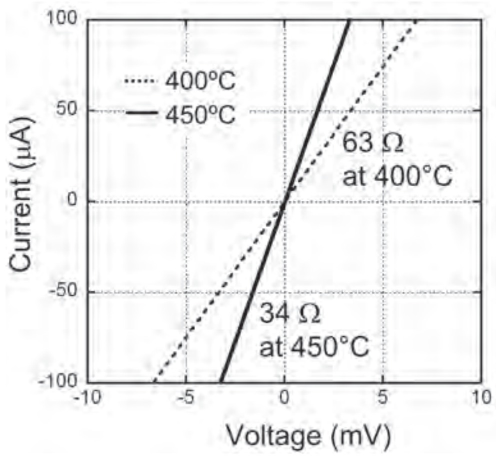
(b) (c)

Fig. 6. TEM images of MWNTs grown at (a) 450, (b) 400, and (c) 365°C.

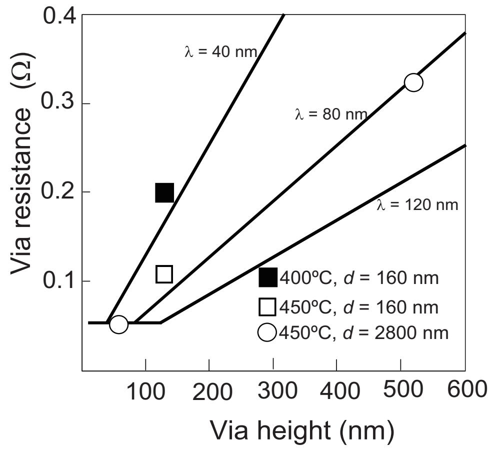
3.3 *Electrical properties of CNT vias*

The resistances of 160 nm CNT vias were measured with a four-point probe using Kelvin patterns. The current-voltage characteristics are shown in Fig. 7(a). It was found that the resistances depend on the growth temperature. The via resistances were 34 Ω for a growth temperature of 450°C and 64 Ω for 400°C. Since the site density of the CNTs was estimated to be about 3.0×10^{11} cm^{-2} for both temperatures, it is considered that the difference in resistance is caused by the difference in CNT quality. The resistance obtained at 450°C is of the same order as that of W plugs. Recently, a resistance of 450 Ω at a low voltage for a CNT via with a width of 300 nm has been reported by another research group,[19] which is, however, not as good as our resistances above.

Figure 7(b) shows via resistance as a function of via height. Results include data for vias with a diameter of 2,800 nm, and all the data are normalized to a diameter of



(a)

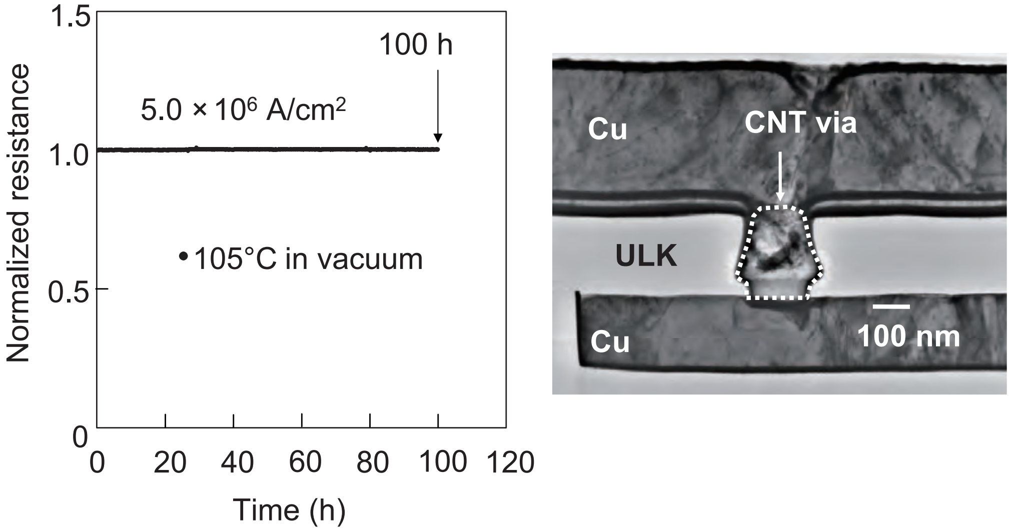


(b)

Fig. 7. (a) Current-voltage characteristics of 160 nm CNT vias. (b) Via resistance as a function of via height. The data are normalized to a via diameter, *d*, of 2800 nm. The solid lines indicate the via resistance obtained by assuming various ballistic lengths for CNTs, λ.

2,800 nm. Solid lines indicate the via resistances obtained by assuming various ballistic lengths for CNTs. As can be seen in the figure, the data points for 450°C fall on the line for a ballistic length of 80 nm. On the other hand, the resistance for 400°C falls on the line for a ballistic length of 40 nm, suggesting that the quality of CNTs grown at 400°C is not as high as the quality of CNTs grown at 450°C, as can also be deduced from the SEM and TEM results. The ballistic length of 80 nm at 450°C is about the same as the via height for LSIs of the hp 32 nm technology node.

The stability of the via resistance at an electric current density of 5.0×10^6 A/cm^2 is shown with a cross-sectional TEM image in Fig. 8. The via diameter and growth temperature were 160 nm and 400°C, respectively. The dielectric layer was made of SiOC with k = 2.6 (referred to as "ULK"). The measurement was performed at 105°C in a vacuum. The resistance remained stable even after running the electric current for 100 h. This indicates that the CNT via is robust over a high-density current as expected. The robustness of CNT vias demonstrated here, however, is still similar to that of Cu. This is mainly because the MWNTs filled only part of the space in the via hole. We expect that CNT vias with a higher CNT density will be much more robust than Cu vias. Incidentally, the via shape looks deformed in the TEM image, which is actually caused by high-energy electrons during the TEM observation. Although the ULK is vulnerable to heat, we found that it is not damaged during CNT growth owing to our low growth temperature.



(a) (b)

Fig. 8. Stability of the via resistance at an electric current density of 5.0×10^6 A/cm^2. A cross-sectional TEM image of the CNT via is also shown.

4. Conclusions

We fabricated carbon nanotube (CNT) via interconnects at low temperatures and evaluated their robustness over a high-density current. CNT vias were fabricated using a new approach, including the use of preformed catalyst nanoparticles, instead of using a conventional catalyst film, to grow MWNTs. This new approach allowed MWNTs to be grown from via holes with diameters as small as 40 nm. We also succeeded in growing MWNTs at temperatures as low as 365°C. The resistance of a 160-nm-diameter CNT via with a growth temperature of 450°C was of the same order as that of W plugs. The ballistic length of CNTs synthesized at 450°C was 80 nm, which is equivalent to the via height of LSIs for the hp 32 nm technology node. The resistance of CNT vias is expected to decrease further with increasing probability of MWNT growth from catalyst particles. Moreover, the CNT vias were able to sustain a current density as high as 5.0×10^6 A/cm^2 at 105°C for 100 h without any deterioration in their properties.

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