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Electrical Properties of Carbon Nanotube Bundles for Future Via Interconnects

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We have developed carbon nanotube (CNT) vias consisting of about 1000 tubes using thermal chemical vapor deposition (CVD) at a growth temperature of 450 °C with cobalt catalysts, titanium carbide ohmic contacts, and tantalum barrier layers on copper wiring. The lowest resistance obtained was about 5 Ω/via. The total resistance of the CNT via was three orders of magnitude lower than that of one CNT, indicating that the current flows in parallel through about 1000 tubes. No degradation was observed for 100 hours at via current densities of 2 × 10⁹ A/cm², which is favorably compared with Cu vias.

Key words: carbon nanotube, chemical vapor deposition, via, interconnect, resistance

1. Introduction

Carbon nanotubes (CNTs) are attractive as nanosize structural elements from which devices can be constructed by bottom-up fabrication. Carbon nanotubes exhibit not only a unique nanoscale structure but also interesting physical properties, such as the ability to be either metallic or semiconductive, depending on the twist or chirality of the tube. They offer unique electrical properties such as current densities exceeding 10⁹ A/cm², thermal conductivity as high as that of diamond, and ballistic transport along the tube. They have been reported to be potentially useful as wiring materials. Even with the current limitations on device dimension, LSI circuits have problems that originate from stress and electro-migration that occurs in copper interconnects, particularly in vias and their surroundings. One potentially effective solution to these problems is to use a CNT, which has a large migration tolerance, as a via. It is difficult, however, to obtain sufficient current for LSI interconnects when using only one CNT. We have therefore explored the feasibility of using bundles of metallic CNTs as a wiring material for future LSI interconnects.

Thus far, we have demonstrated CNT vias directly on a Ni-silicide layer; the vias can be used as electrodes for metal-oxide-semiconductor field-effect transistors (MOSFETs). In this study, we grew vertically aligned multiwall nanotube (MWNT) bundles selectively in via holes on copper wiring using thermal chemical vapor deposition (CVD) at a growth temperature of 450 °C and measured the electrical properties of MWNT bundles to preliminarily demonstrate the presence of CNT vias.

2. Experimental

Figure 1 is a schematic of the CNT via process. The fabricated substrate consists of a copper wiring (100 nm), a tantalum barrier layer (5 nm), a titanium contact layer (2.5 nm), a cobalt catalyst layer (2.5 nm), and a SiO₂ dielectric layer (350 nm) using tetraethylorthosilicate (TEOS) CVD. Via holes were patterned using conventional photolithography and anisotropic dry etching with fluorine-based gases. The titanium contact layer and cobalt catalyst layer were formed on the bottom of via holes by the lift-off process using photo-resist and electron beam evaporation.

We grew bundles of MWNTs selectively in via holes using thermal CVD with a cobalt catalyst. Low resistance ohmic contact to the lower copper wiring was simultaneously formed due to the titanium contact layer. When the catalyst layer is very thin, like the 2.5-nm cobalt layer, the metal diffusion between the catalyst and copper makes it hard to grow MWNTs directly on copper. The tantalum barrier layer suppressed this metal diffusion and enabled us to grow MWNTs on a copper layer. After the titanium contact layer (50 nm) and an upper copper wiring (100 nm) were connected to the CNT vias, we performed two-terminal current-voltage measurements on 1000 via chains.
CNT growth technology cannot be used in Si LSIs unless the growth temperature can be kept below 450°C, a limit established by the thermal tolerance of low-k dielectrics. At first, we tried to realize this requirement using hot-filament CVD (HF-CVD). Before the HF-CVD growth, the substrate was heated to 510°C and cleaned for 10 min in H₂ gas at 1 kPa. A mixture of C₂H₂, Ar and H₂ was then introduced as the gas source. The pressure in the CVD chamber was set to 1 kPa, the hot filament 6 mm above the substrate was turned on, and MWNT growth occurred. The stage temperature was set to 510°C, but the heat radiated from the filament (which had a temperature above 2000°C) increased the substrate temperature to 600°C during the 10-min MWNT growth period. We could lower the growth temperature to 450°C by thermal CVD without a hot-filament. Before the thermal CVD growth, the substrate was heated to 450°C and cleaned for 10 min in H₂ gas at 1 kPa. A mixture of C₂H₂ and Ar was then introduced as the gas source. The pressure in the CVD chamber was set to 1 kPa, and MWNT growth occurred for 40 min.

3. Results and Discussion

Figure 2(a) shows a scanning electron microscopy (SEM) image of CNT vias formed by thermal CVD at a growth temperature of 450°C. We have succeeded in growing vertically aligned MWNT-bundles in via holes about 2 μm in diameter. Figure 2(b) shows a transmission electron microscopy (TEM) image of a MWNT in a hole. We could grow MWNTs with an outer diameter of about 10 nm and with well-graphitized graphen sheets. The electrical properties of these MWNTs were suitable for wiring materials. In our previous study, we investigated a CNTs/titanium-contact-layer interface to clarify the growth mechanism. Although a film catalyst was used, we observed catalyst nanoclusters with a diameter of approximately 10 nm on the surface of the titanium contact layer using TEM. MWNTs with catalyst nanoclusters inside the roots of the CNTs grew vertically on the titanium contact layer. In a word, the film catalyst changed to the nanoclusters during the growth, and these catalyst nanoclusters play an important role in determining the CNT diameter.

We also estimated from high resolution SEM that the packing density of CNTs was roughly on the order of 10¹⁰/cm², which corresponds to about 1000 tubes in 2-μm-diameter via holes.

Figure 3 shows the results of two-terminal current–voltage measurements for 1000 via chains about 2 μm in diameter. The current increased linearly depending on the voltage, which means that good ohmic contacts have been realized between CNT-bundles and the electrode. The resistance of one CNT via consisting of about 1000 tubes was 5 Ω at a voltage of 100 mV and at room temperature. The measured resistance includes the contact resistance of CNT-bundle/metal-electrode interface and the tube resist-
ance. The dependence of the via resistance on number of CNTs is shown in Fig. 4, which also shows the resistance of one CNT and three CNTs bridging the gap between 10-nm-nikel/100-nm-titanium electrodes, and CNT vias consisting of about 1000 tubes between lower and upper 10-nm-nikel/100-nm-titanium electrodes at a growth temperature of 600°C.8,10 In the case of 10-nm-nikel/100-nm-titanium electrodes, the total resistance of the CNT via was 100 Ω, which is three orders of magnitude less than that of one CNT. As previously mentioned, we estimated from SEM observations that the number of CNTs in via holes was about 1000 tubes. In the case of MWNT, the tube’s conductivity always seems metallic, because the tube diameter is large enough to be metallic at room temperature. These data indicate that the current flows in parallel through all 1000 metallic tubes. We have decreased the via resistance using a cobalt catalyst, a titanium carbide ohmic contact, and a tantalum barrier layer on copper wiring. The lowest resistance of about 5 Ω is one order of magnitude greater than the resistance of a 2-μm-diameter via with tungsten, and two orders of magnitude greater than that of one filled with copper. It is important to produce smaller-diameter nanotubes that pack more densely. We are therefore going to try a catalytic nano-particle technique to increase the current roughly 10^10/cm^2 packing density of the nanotubes to 10^12/cm^5.

Figure 5 shows preliminary results of the reliability of CNT vias consisting of about 1000 tubes at a growth temperature of 600°C.11 No visible degradation occurred at a via of 2.0 × 10^8 A/cm^2 for 100 hours at room temperature. This current is comparable to the higher current density in copper vias, which is limited due to electro-migration. In this case, the estimated current density of one CNT is about 2.0 × 10^8 A/cm^2, which is two orders of magnitude higher than the current density for copper.

![Image of CNT density vs number of CNTs](image)

**Fig. 4.** Dependence of the total resistance of CNT vias on the number of CNTs.

**Fig. 5.** Dependence of the two-terminal current of a CNT via on testing time.

### 4. Conclusions

We have measured the electrical properties of CNT vias consisting of about 1000 tubes between the lower and upper copper wiring. We could lower the growth temperature of CNTs to 450°C. The total resistance of the CNT via was three orders of magnitude lower than that of one CNT, indicating that the current flows in parallel through about 1000 tubes. This result will enable us to fabricate CNT vias with a low resistance and a large migration tolerance for future LSI interconnects.

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