Selective deposition of catalyst nanoparticles using the gravitational force for carbon nanotubes interconnect

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Abstract

The photolithography process has generally been used for the making of catalyst layers used for the synthesis of CNTs due to its comparative ease. However, this method results in the formation of undesirable catalyst particles, which deteriorate the quality of the devices. Therefore, we tried to form a catalyst layer without using any lift-off or wet etching process, especially for the formation of carbon nanotube interconnects. After spin coating the samples, which were previously fabricated with several vias, with an iron-acetate solution, the catalyst layer was pulled down into the bottom of the holes through the force of gravity. We were able to remove the catalyst layer which was coated over undesirable areas, by TMAH (tetramethylammonium hydroxide, N(CH₃)₄OH) treatment. After the catalyst deposition process, we synthesized CNTs and observed them by scanning electron microscopy (SEM).

Keywords: CNT interconnect; Iron acetate; Chemical vapor deposition (CVD)

1. Introduction

There has been considerable development in both the production and application of carbon nanotubes (CNTs) since their discovery in 1991 [1], and CNTs have received considerable attention due to their unique physical and chemical properties [2,3]. Their unique electrical properties, such as their high current density exceeding 10⁹ A/cm² [4,5] and ultrahigh thermal conductivity as high as that of diamond [6], are of particular interest for electronic devices such as CNT-FEDs (field emission devices), CNT interconnects, etc. Recently, many attempts have been made to synthesize CNTs using nanoparticle catalysts [7–14]. Among the numerous potential applications of CNTs, intensive research has been conducted into their use as interconnects [15–17]. The interconnect in an integrated circuit (IC) distributes the clock and other signals, as well as providing power or ground to the various circuits on a chip. The International Technology Roadmap for Semiconductors (ITRS) [20] emphasizes the high-speed transmission needs of integrated circuits as the motivation for future interconnect development.

The size of interconnects in ultra large-scale integrated circuits (ULSIs) is gradually decreasing. This scale reduction of the copper material which is now being used as an interwiring conductor in ULSIs results in an increase in the resistance, because the electrical resistivity of Cu increases with decreasing dimensions of the interconnect, due to the effects of electron surface scattering and grain boundary scattering [18–20].

As stated above, the shrinkage of the feature size will inevitably result in an increase of the copper resistivity, due to surface and grain boundary scattering, as well as aggravating the surface roughness. In contrast, CNTs exhibit the ballistic flow of electrons with electron mean free paths of several microns, and are capable of conducting very large current densities. Therefore, CNTs have been proposed as potential candidates for power and signal interconnection. The extraordinary electrical, mechanical, and thermal properties of CNTs may provide near-term solutions for problems in interconnects in silicon IC technology. For example, Wei et al. [5] showed that...
the current carrying capacity of multiwalled CNTs (MWCNTs) did not degrade after 350 h at current densities of $10^{10} \text{ A/cm}^2$ at 250 °C. The thermal conductivity of CNTs [21,22] is about $1700 – 3000 \text{ W/m K}$. The mechanical properties of CNTs are also superior to those of the traditional materials used in the IC industry.

In this study, we investigated a potential method of depositing the catalyst particles required for the growth of CNTs, without resorting to the traditional PVD (physical vapor deposition) method and lift-off process, especially in a CNT interconnect system.

2. Experimental

The organo-metallic materials containing transition metals used for CNT synthesis are dissolved in organic solvents such as ethanol, and coated on a substrate by the dip-coating or spin-coating method. A solution containing catalyst particles is easy to handle and does not require complex systems to coat it. However, in the case where nanoparticles are used instead of a thin film, there are several problems with respect to the uniformity of the particle distribution that need to be considered.

We made an iron-acetate solution as a catalyst. Iron-acetate $[(\text{C}_2\text{H}_3\text{O}_2)_2\text{Fe}]$ powder (Aldrich; 95%) was weighed and dissolved in ethanol (Fisher Scientific; 99.9%). Ethanol has good solubility for metal acetates. However, it was not easy to use ethanol alone as a solvent, due to its high vapor pressure and low viscosity at room temperature, which made it difficult to make a uniform thin film, due to the agglomeration of the catalyst particles during the drying process. Therefore, ethylene glycol was added to obtain a solution with low vapor pressure and high viscosity. Ethylene glycol slightly dissolved the iron acetate. The molar concentration of iron acetate, and the volume ratio of the two solvents were experimental parameters used to control the surface concentration of the catalyst. Special attention was paid to the number density of the CNTs, which is an important issue in the CNTs interconnect system.

The SEM images of the SiO$_2$ via holes are shown in Fig. 1. The metal layer TiN (100 nm) film on the silicon substrate was deposited by the sputtering method. Titanium nitride is useful as the adhesion layer for CNT vias. Furthermore, titanium nitrate
has been widely used as the barrier metal for Cu vias in VLSIs. A 30 nm-thick-SiO$_2$ film was deposited on the metal layer (TiN) by the PE-CVD method and the via-patterns were made by reactive ion etching method.

After spin coating the sample, previously fabricated with a large number of vias, with iron-acetate solution, the catalyst layer was pulled down into the bottom of the holes by gravity. That is, the iron-acetate solution was spin coated onto the samples which having several vias. In that case, the catalyst layer was formed onto the whole area of the sample. To position the catalyst on the bottom of the holes, we put the sample on the level surface (a horizontal plane) before the drying process. Then, the catalyst layer could be pulled down into the bottom of the holes by gravity. This mechanism was used to form a catalyst layer at the bottom of the holes in our process. And we found that the catalyst layer in our experiment was selectively dissolved by TMAH (tetramethylammonium hydroxide, N(CH$_3$)$_4$OH) solution. Therefore, we were able to remove the catalyst layer which was coated over undesirable areas, especially outside of the holes. That is, due to the chemical reaction of the Fe$^{2+}$ ions in iron acetate and OH$^-$ ions in TMAH, the catalyst layer was removed in the form of Fe(OH)$_2$. Actually, the first exposed photo-resist (PR) layer was removed by TMAH, and then the catalyst layer was removed by the same TMAH solution. This mechanism of patternability has been reported in detail elsewhere [7,8].

The catalyst coated substrate was transferred into the CNT growth chamber and was heated to 550 °C and then sustained at this temperature for 30 min in CO (0.1 slm) and H$_2$ (1.25 slm) ambient. The substrate and grown CNTs were analyzed by field emission scanning electron microscopy (FE-SEM, A0344, Philips).

3. Results and discussion

Fig. 2A shows the processing steps used for the preparation of the sample. After spin coating the sample, which was previously fabricated with a large number of vias, with iron-acetate solution, the catalyst layer was pulled down into the bottom of the holes by gravity before the drying process. This process enables use to make an exceedingly thick catalyst layer on the SiO$_2$ layer. After the catalyst layer was pulled down by gravity, the substrate was treated with TMAH solution, a typical alkali-based solution. Iron acetate reacted with the TMAH solution through an acid–base reaction and was dissolved into solution. As mentioned above, the Fe$^{2+}$ in iron acetate undergoes a chemical process through the action of the base, OH$^-$, in TMAH.

During the TMAH treatment, the catalyst layer which was pulled down to the bottom of the holes did not react with the
OH⁻ ions in the TMAH solution due to the high surface tension of the TMAH solution. The TMAH treatment was conducted with concurrent rinsing at a spin-coater speed of 3000 rpm, and these conditions led to our experimental result. Fig. 2B shows the SiO₂ via surface after the TMAH treatment. No catalyst elements were observed except on the inside of the vias.

Before the growth step, the sample was loaded in a vacuum oven and annealed at 350–400 ℃ in air to burn the organic compounds. The decomposition conditions were investigated using thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). It was found that iron acetate was changed into iron oxide in air, or into iron carbide in nitrogen ambient by thermal decomposition.

Fig. 3 shows the plane-view SEM images of the grown CNTs from the several vias. The CNTs could be grown only from the inside of the holes. That is, there was a selective reaction with the TMAH solution on the catalyst layer which was coated on the substrate. This implies that all of the catalyst layer which was located over the holes was drawn down by the force of gravity. We could not observe any CNTs outside of the holes.

The parameters of this process were the viscosity of the solution and speed of rotation of the spin coater which was used for the formation of the catalyst layer. These parameters are also related to the number density of the CNTs, which is one of the important aspects of the CNT interconnect system. By controlling the viscosity and molar concentration of the solution and the spin-coater speed, we can control the characteristics of the catalyst layer, such as the number density and diameter of the CNTs.

We also confirmed the effect of the TMAH treatment through the preparation of two different samples with and without the TMAH treatment. We found that the sample, which was not treated with the TMAH solution, was coated over the whole area by iron acetate. That is, the sample was coated by the catalyst material on the outside of the holes, rather than being coated selectively inside the holes. Therefore, the whole area of the sample was covered with CNTs.

Fig. 4 shows the plane-view SEM images of the CNTs grown from the iron-acetate [[(C₂H₃O₂)₂Fe] films on the Si substrate with TMAH treatment (a) and without TMAH treatment (b). In comparison with the sample shown in Fig. 4B, in which the CNTs were synthesized from both the inside and outside of the holes, it can be seen in Fig. 4A that the CNTs were selectively synthesized only from the inside of the holes. These images demonstrate that only the catalyst layer which was coated on the outside of the holes was removed by the TMAH treatment.

We will be performing current–voltage measurements on the CNTs interconnect as the next step, in order to examine the resistance and determine the proper density of CNTs and their diameter, etc. Metals 1 and 2 (i.e. the bottom and top electrodes) will be connected by CNTs vias which were obtained by optimizing the height of the CNTs through the adjustment of the growth time or CMP (Chemical Mechanical Polishing) process, thus allowing for the overgrowth of the CNTs over the vias.

4. Conclusion

We made an iron-acetate solution as a catalyst by dissolving iron acetate in ethanol and dissolving it again in ethylene glycol. After spin coating the samples having several vias with iron-acetate solution, the catalyst layer was pulled down into the bottom of the holes by gravity. We found that the catalyst layer in our experiment was selectively dissolved by TMAH solution. In this way, we could remove the catalyst layer coated over undesirable areas. Using this method, we could selectively synthesize CNTs for use in the CNTs interconnects systems.

Acknowledgements

This work was supported by the Korean Ministry of Commerce, Industry and Energy through the Samsung Advanced Institute of Technology and also by the National R&D Project for Nano Science and Technology.

References