

Doped Carbon Nanotubes for Interconnects

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Abstract

The development of high conductivity, high density carbon nanotube forests for via interconnects is described.

Introduction

Sp² carbon is the only material able to conduct current densities up to 10⁹ A/cm² as desired for future interconnects. However, the quantum of resistance of carbon nanotube (CNT) based interconnects means that contact resistance will limit the overall conductivity unless they are made with high packing density. In addition, we must integrate them in a way compatible with general CMOS processing, and allow both metallic and semiconducting CNTs to contribute to the conductivity. We show here the components of a low resistivity CNT interconnect technology.

Growth

CNTs must be grown in the via holes by catalytic chemical vapor deposition (CVD) [1]. A thin metal film catalyst (such as Fe or Co) naturally converts into the active catalyst nanoparticles by de-wetting if the under-lying substrate layer has a low surface energy, as the metal has a high surface energy. Thus, ultra-high density CNT forests (10¹³ cm⁻²) were grown on insulating oxides like Al₂O₃ because of their low surface energy [2-5]. However, metallic substrates are generally difficult to grow on because of their high surface energy and their reactivity with hydrocarbons or oxygen [1]. This led to use of TiN or Ta based support layers, or CoSi₂ or ZrN [6-8]. However, these materials produce lower density forests than Al₂O₃ [6-9].

TiSiN (and TaSiN) has been found to be the ideal conductive substrate layer for CNT growth because it is metallic, amorphous, refractory (non-reactive) and with low surface energy [6]. The low surface energy arises from its mixed covalent/ionic bonding, and this encourages catalyst de-wetting (Fig. 1). The amorphous character means an absence of grain boundary diffusion pathways that allow catalyst atoms to diffuse inwards from the surface and so degrade yield. In addition, the deposition of a nominal 0.1 nm thick discontinuous Al₂O₃ overlayer on the catalyst discourages lateral catalyst diffusion and sintering. The combination of these factors allows growth of CNTs with an area density of 5.1x10¹² cm⁻², the highest ever achieved on metals and close to that achieved on Al₂O₃ (Fig 2)[6]. A 0.4 nm Fe thick catalyst was used at 600C in 10 sccm C₂H₂ and 500:1000 sccm H₂:Ar. Co will be used in future to lower growth temperature.

Doping

In a SWNT forest of random chirality, only 1/3 of tubes are metallic, the rest are semiconducting, and effectively wasted for interconnect applications. Such forests can be doped by eg FeCl₃ or SOCl₂. However such chemicals are unstable as dopants. We have studied doping by MoO₃. This is a degenerate semiconductor oxide when solid, with an unusually high work function of 6.6 eV. It can be evaporated as a small inorganic molecule and it converts into a layered solid when condensed. It dopes by charge transfer. It was recently used to produce stable p-type electrodes for OLEDs and as a p-type dopant of graphene layers [10]. For CNTs, the basis of doping is to push E_F over the van Hove singularities associated with semiconducting SWNTs, so that all tubes can conduct.

In our experiments, MoO₃ was evaporated onto CNTs lying horizontally after treatment with IPA (Fig 3). Resistivity is measured by 2-point probe. A plot against CNT bundle length is given so as to extract contributions from contact resistance if necessary (Fig 4). The 2-terminal conductivity of the mats is found to increase by a factor of ~20 by this doping. The stability of doping was checked by conductivity and XPS band shift measurements. Overall resistivity values are compared in Table 1 where it is seen that the doped CNTs are 10 times that of copper.. A schematic of doping by MoO₃ is shown in Fig 5.

Integration

CNT forests grown in 1.5-2.5 μm via holes in 2 μm thick TEOS derived SiO₂ were grown on TiN substrates (Fig 6), and a 3 to 5 nm thick Fe catalyst was used with growth at 500C. These catalyst conditions are not expected to produce very high density forests yet, but as a demonstration of capability. Al top contacts were applied, without chemical mechanical polishing. Resistivity was measured between metal lines, and our resistivity values are seen to be comparable with many of better ones in the literature (Fig 7). This suggests that there are no contact problems in this processing. Substitution of TiSiN for TiN substrate layer will increase grown densities, and the application of doping should therefore led to a resistivity lowered by a factor of x20 compared to the presently achieved values.

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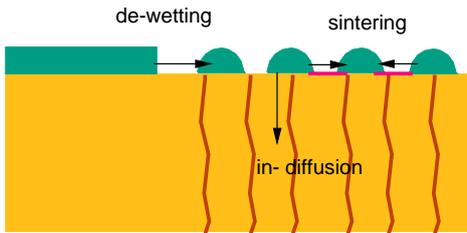


Fig. 1. TiSiN support layer enables de-wetting by as low surface energy, and its amorphous character without grain boundaries inhibits catalyst in-diffusion, and Al₂O₃ top layer stops sintering.

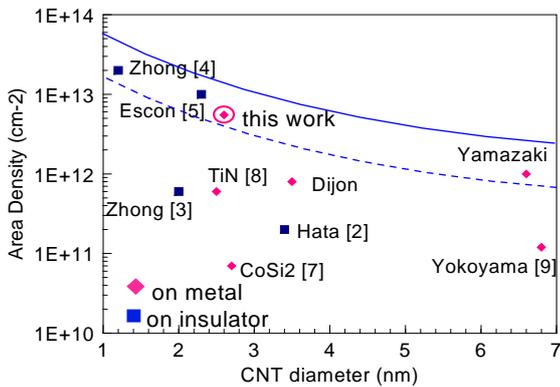


Fig. 2. CNT Area density vs CNT diameter for various CNT forests grown by CVD, compared. On metal and on insulator [2-9].

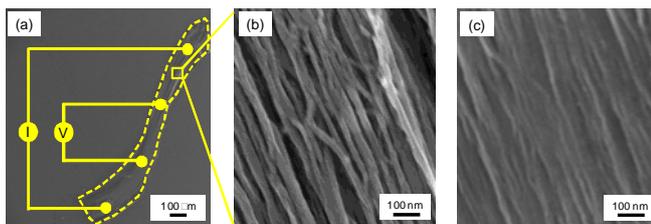


Fig. 3. CNT forest, liquid induced compacted sample, and electrical measurement after doping.

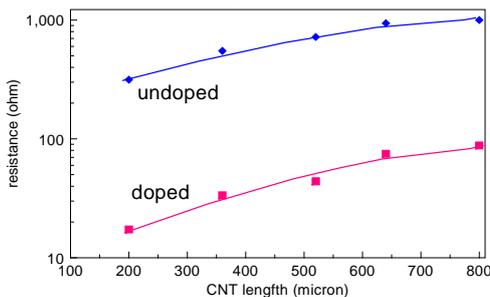


Fig.4. Effect of MoO₃ charge transfer doping on CNT bundle resistivity.

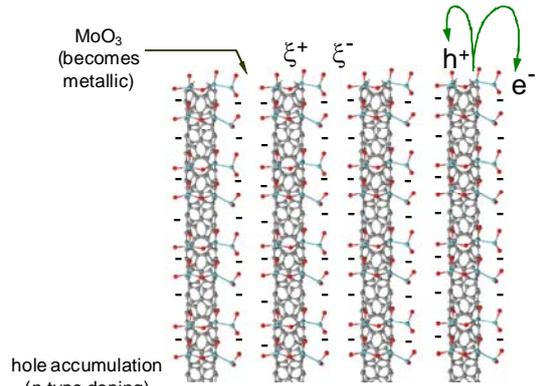


Fig 5. Schematic of doping by MoO₃.

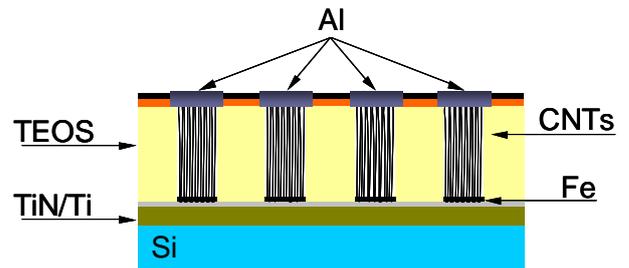


Fig. 6. Process steps for CNT growth in Vias, and metallisation.

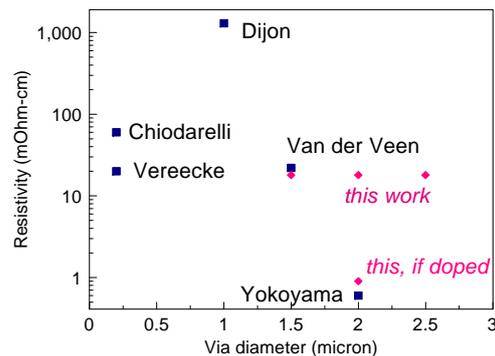


Fig. 7. Comparison of our measured in-Via resistivities, compared to state of art literature values [11-14]. Also included is an expected resistivity, if higher density CNTs were grown by using TiSiN than TiN, and by doping the CNTs.

Table. 1. Comparison of resistance values

	Ω cm
Undoped forests	1.4 10 ⁻³
Doped forests	1.2 10 ⁻⁵
Pristine graphite	3.6 10 ⁻³
10 layers graphite	4.1 10 ⁻⁶
copper	1.6 10 ⁻⁶