Growth of vertically-aligned carbon nanotube forests on conductive cobalt disilicide support
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I. INTRODUCTION

Carbon nanotubes (CNTs) have been widely investigated for their novel electronic properties and potential applications. Due to their very high current-carrying capacity of \( \sim 10^9 \) A/cm\(^2\),\(^2\) thermal conductivity of up to 6600 W/m K,\(^2\) and chemical stability, there has been considerable effort to introduce them as replacements for Cu interconnects beyond the 22 nm node of the semiconductor roadmap.\(^3\)-\(^7\) The advantage of CNTs is that they can be grown in high aspect ratio vias and do not require the diffusion barrier liners. For this application, the nanotubes must be grown by catalytic chemical vapor deposition (CVD) at a high packing density with an electrically conductive substrate underneath the growth catalyst in order to minimize the contact resistance. Although the growth of CNT forests on metallic substrates has been demonstrated before, the catalyst and CNTs are usually on insulating support layers such as Al\(_2\)O\(_3\) or SiO\(_2\).\(^8\)-\(^14\) There are many fewer reports of nanotubes grown on metal supports.\(^4\),\(^15\)-\(^21\) It has proved very difficult to obtain similar growth of dense, vertically-aligned nanotube forests on conducting support layers. Some of the previous reports were on metals not compatible with microelectronics\(^16\) and some gave relatively low nanotube densities or disordered horizontal networks or “spaghetti.”\(^17\),\(^18\) To prove the viability of CNTs for interconnects, it is necessary to demonstrate growth of vertically-aligned arrays of single-walled or small diameter multiwalled nanotubes on a metallic support layer with a high density of order \( 10^{13} \) cm\(^{-2}\).\(^4\),\(^6\),\(^21\)

The state of the catalyst is critical in CNT growth processes. In order to be catalytically active, the as-deposited catalyst thin film must be transformed into high surface area nanoparticles. The catalyst-support interaction controls this transformation and in the resulting catalyst particle size distribution. Catalyst films dewet from the support layer on annealing with the transformation driven by the difference in surface energy between the metal catalyst and the support layer with a contact angle \( \theta \)

\[
\gamma_s = \gamma_c + \gamma_{sc} \cos(\theta) \tag{1}
\]

where \( \gamma_s \) is the support surface energy, \( \gamma_c \) is the catalyst surface energy, and \( \gamma_{sc} \) is the catalyst-support interface energy. Most oxide supports have a low surface free energy and, therefore naturally induce the dewetting of the higher surface energy metals. However, if the support is also a metal with a high surface energy, it is less easy to dewet the catalyst.\(^17\)

The surface energies of various metals are tabulated in Table I, based on experimental data, models or

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Metal & \( \gamma_s \) & \( \gamma_c \) & \( \gamma_{sc} \) & References \\
\hline
Ni & 2.08 & 2.01 & 22, 25 \\
Co & 2.22 & 2.77 & 22, 25 \\
Fe & 2.12, 1.72 & 2.22 & 22, 23, 25 \\
Mo & 2.51 & 3.45 & 22, 25 \\
Cr & 2.00 & 3.5 & 22, 25 \\
W & 2.76 & 4.0 & 22, 25 \\
Ta & 2.49 & 3.08 & 22, 25 \\
Ti & 1.75 & 2.52 & 22, 25 \\
TiN & 1.6, 1.40 & Marlo 28, 43 \\
ZrSi\(_2\) & 0.8–1.2 & D’Heurle 29 \\
TiSi\(_2\) & 0.8–0.9 & D’Heurle 29 \\
CoSi\(_2\) & 0.72–0.8 & 1.65 & Yao 30, 43 \\
NiSi\(_2\) & 1.13 & 43 \\
SiO\(_2\) & 0.043–0.106 & Sun 25, Iler 26 \\
Al\(_2\)O\(_3\) & 0.062–0.1 & 0–0.1 & Sun 25, Norskov 27 \\
MgO & 0.1 & Sun 25 \\
\hline
\end{tabular}
\caption{Surface energies of solid metals, metallic compounds, and oxides in J/m\(^2\). [Data of Tyson and Miller (Ref. 22) are for liquid metals, multiplied by a constant factor of 1.18 to give values for the solid. The values of Vitos et al. (Ref. 24) were calculated by density functional theory, for the lowest energy face of the crystalline phase.]}\end{table}

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The catalytic metals Fe, Co, and Ni have surface energies ranging from 2.08 to 2.22 J/m², in contrast to oxides with surface energies of 0.06 to 0.1 J/m² for SiO₂ and 0 to 0.2 J/m² for Al₂O₃. As possible metallic support layers, the refractory transition metals have surface energies ranging from 2.49 J/m² for Ta, 2.77 J/m² for W to 2.51 J/m² for Mo. It is, therefore, interesting to consider other alternatives. Indium tin oxide gave large diameter nanotubes, which would be unsuitable for vias. TiN has a surface energy of 1.6 J/m² and is much lower than the simple transition metals. CoSi₂,30,43 much lower than the simple transition metals. We compare the surface morphology changes in CoSi₂/Fe with two other commonly used substrate/catalyst systems for vertical CNT growth (Al₂O₃/Fe and SiO₂/Fe) (Ref. 14) and we show that CoSi₂ is a useful candidate compared to SiO₂ and Al₂O₃ to support CNT growth for interconnect applications.

II. EXPERIMENTAL

CoSi₂ was prepared by a rapid thermal annealing process on a Si/Co/TiN structure, followed by etching away the TiN capping layer and any residual Co.31,32 The processes produced a ~20 nm thick CoSi₂ layer on top of the silicon wafer. For comparison, we also used both n-type silicon (100) wafers with 200 nm thermally grown SiO₂ and similar Si/SiO₂ wafers covered with a 10 nm sputter deposited Al₂O₃ film. A 1 nm thick Fe catalyst layer was sputtered on top of these three substrate systems. The samples were then loaded into a 2 inch diameter quartz tube furnace and heated to 650 °C under 1000 SCCM (SCCM denotes cubic centimeter per minute at STP) Ar at atmospheric pressure. The samples were either kept at this temperature for 15 min under 400 SCCM Ar or were directly exposed to a reducing atmosphere of 200/500 SCCM Ar/H₂ to reduce Fe oxides, and enable the catalyst restructuring and activation.33,34 10 SCCM C₂H₂ was subsequently introduced to grow CNTs. No plasma aided restructuring was used. After growth, the samples were cooled to room temperature in 200 SCCM Ar. Structural investigations of CoSi₂ film were carried out using a Bruker axis D8 advance x-ray diffractometer (XRD) in Bragg–Brentano θ-2θ geometry (x-ray source: 1.541 Å, 2-θ measured over 15°–85°).

III. RESULTS AND DISCUSSION

FIG. 2. (Color online) XRD scans of CoSi₂ samples after different process stages. The bottom scan shows a bare Si substrate for reference, the identification of the CoSi₂ (220) reflection follows (Ref. 36)
tative assessment of the structural stability of the CoSi$_2$. Both after annealing and after growth of CNTs, there are no additional reflections due to phase changes in the film such as, formation of carbides, oxides, etc. nor is there a change in position or relative intensity of the (220) reflections. This implies that the crystalline structure of the CoSi$_2$ layer is neither affected by the annealing supporting the AFM analysis in Fig. 1) nor by the CVD process steps.

Figures 3(a) and 3(b) compare the surface roughness of CoSi$_2$/Fe layers after a 3 min and 18 min anneal at 650 °C in the 200/500 SCCM Ar/H$_2$ gas mixture. Figure 3(c) shows typical line scans taken from these images, showing a surface roughness of a much shorter lateral length scale than that of the CoSi$_2$ alone [Fig. 1(c)]. This indicates that the Fe film has formed into a series of nanoparticles. After an 18 min anneal, the lateral and vertical length scales of the roughness remains similar [Fig. 3(b)]. This means that the CoSi$_2$-supported Fe nanoparticles do not undergo further sintering during annealing at 650 °C. This suggests that the lateral diffusion of Fe on CoSi$_2$ is quite slow at 650 °C.

Figure 4 shows for comparison the surface roughness of Al$_2$O$_3$/Fe films after 3 min and 18 min annealing at 650 °C in the Ar/H$_2$ gas mixture and the associated line scans. The Fe forms a series of nanoparticles with a lateral length scale of about 3 nm, as we found previously. Figure 4(b) shows that, after an additional 15 min thermal annealing at 650 °C, there is only a slight increase in the number of observable Fe particles compared to after 3 min annealing. The line scans in Fig. 4(c) confirm that the surface roughness remains reasonably small and the particle size, measured from the height of the line scans, does not change significantly. This indicates that Fe is immobile on Al$_2$O$_3$ at 650 °C and so does not sinter.

Figure 5 shows a surface roughness image of Fe supported on SiO$_2$ after annealing for 3 min and 18 min in 200/500 SCCM Ar/H$_2$ at 650 °C. After 3 min anneal, the Fe film has broken up into nanoparticles with a narrow diameter distribution centered on 10 nm [Figs. 5(a) and 5(c)]. After the 18 min anneal at 650 °C, the particle diameter distribution has widened to 3–35 nm [Figs. 5(b) and 5(c)]. This means that the SiO$_2$-supported Fe particles begin to agglom-
erate at 650 °C and 18 min annealing causes severe sintering of catalyst particles and finally creates many large (~35 nm in diameter) particles, while many small (~3 nm in diameter) particles remain. Thus, as previously noted, SiO₂ is a worse sintering than Al₂O₃ for nanotube growth, as it allows more sintering of Fe. Our results also suggest that CoSi₂ is a potentially better support than SiO₂ because it inhibits sintering of Fe at 650 °C.

Figures 6(a) and 6(d) show vertically-aligned MWCNTs grown on CoSi₂/Fe and Al₂O₃/Fe, after both short (3 min in 200/500 SCCM Ar/H₂) and long (additional 15 min thermal annealing in 400 SCCM Ar) pretreatments. Dense vertically-aligned MWCNT mats grow on all three substrates subjected to the 3 min anneal [Figs. 6(a), 6(c), and 6(e)]. Dense mats also grow on the CoSi₂- and Al₂O₃-supported Fe catalyst after a further 15 min anneal in Ar [Figs. 6(b) and 6(d)]. In contrast, for SiO₂/Fe, vertically-aligned MWCNTs only grow for the short pretreatment [Fig. 6(e)], whereas long pretreatment produces only a low density, random spaghetti network of MWCNTs [Fig. 6(f)]. Thus, the ability to grow vertically-aligned mats reflects the evolution of catalyst roughness seen by AFM in Figs. 3–5.

The different yields of MWCNTs on these samples (Fig. 6) can be explained by considering the catalyst particle size distributions on the different catalyst support layers. Fe particles supported on CoSi₂ (Fig. 3) and Al₂O₃ (Fig. 4) do not undergo agglomeration under our annealing conditions, the particle size distributions remain narrow after both short and long pretreatments. In contrast, during the pretreatment, SiO₂ supported Fe particles can easily agglomerate and start forming large Fe particles [up to ~35 nm diameter in Fig. 5(b)], at the expense of some smaller ~10 nm Fe particles [Fig. 5(a)]. This results in a very wide size distribution of Fe particles, ~3–35 nm in diameter [Fig. 5(c)]. CNTs grown from very different sized catalyst particles will show very different growth rates.37 This will inhibit the crowding effect and no vertical alignment will be achieved [Fig. 6(f)].

A transmission electron microscopy (TEM) image of a typical MWCNT grown on CoSi₂/Fe and a histogram of the observed diameter distribution and the number of walls of the MWCNTs are shown in Figs. 7(b) and 7(c). The average diameter is 13 nm and the average number of walls is 11. Figure 7(a) shows a high resolution scanning electron microscopy (SEM) image of the base of a nanotube forest grown on CoSi₂/Fe, after the 3 min anneal. A nanotube density of ~5 × 10¹⁰ cm⁻² is estimated, corresponding to a wall density of ~5.5 × 10¹¹ cm⁻². This shows that Fe on CoSi₂ gives a reasonable wall density but for the present growth conditions, it does not reach the highest densities of ~5 × 10¹² cm⁻² achieved by Al₂O₃/Fe in lower pressure growth.12,13

The growth mechanism, tip or root growth, is determined using the interrupted growth method.38 Figure 8 shows an SEM image of a nanotube mat grown from Fe on CoSi₂ after interrupted growth of 2 min followed by 4 min. A growth stripe is seen near the top, which is due to the interruption. The inset shows a close-up of the stripe. As the growth rate is linear, and the stripe is nearer the top, this indicates that growth occurs by root growth. This confirms the observation that higher density, vertically-aligned mats generally require root growth.
IV. DISCUSSION

Our demonstration of growth vertically-aligned CNT mats on CoSi2 indicate the advantages of silicides as conductive support layers for vias and interconnects. CoSi2 and similar silicides are stable, refractory metals. They oxidize only with a parabolic growth law, whereas nitrides such as TiN oxidize with a linear law. The surface free energies of silicides are roughly half that of TiN (Table I), so that catalyst dewetting takes place more easily on silicides. Their melting temperature and refractory character mean that they remain as a smooth surface at the likely nanotube growth temperatures.

In contrast, the refractory elemental metals W and Ta form stable carbides, so that they can become strongly carburised during typical growth conditions. Additionally, Fe tends to alloy with Ta.

At present, the nanotube densities achieve here of $5 \times 10^{10}$ cm$^{-2}$ must be increased and the nanotube diameter decreased for their performance as vias to be good enough. This will involve further additions and optimizations of the pretreatment and growth process, such as oxidative or reducing or plasma pretreatment. Preliminary electrical measurements give a resistance of 2.8 kΩ per tube but this is high because of the poor top contact. Work is in progress to improve this.

The results offer an opportunity to achieve both horizontal and vertical CNT interconnects. The advantage of CNTs for vertical interconnects is that they can grow in high aspect via, which are inconvenient for tungsten plugs or Cu with liners. On the other hand, the greatest advantage of CNTs is in horizontal interconnects, where they can reduce resistor capacitor (RC) time delays. However, the technology for horizontal growth is much less developed at present.

Standard semiconductor processes like self-aligned silicidation allow CoSi2 to be patterned on vertical surfaces, which is essential for the growth of nanotubes as horizontal interconnects but is less easy for Al$_2$O$_3$ or SiO$_2$ or for other conductive substrates such as TiN, which is deposited by sputtering (side-wall atomic layer deposited TiN would be possible).

V. CONCLUSIONS

CoSi2 is found to be a stable, highly conductive support layer for the catalytic growth of CNTs. CoSi2 allows the growth of high density, vertically-aligned MWCNT mats by the root growth mechanism. A CoSi2 support layer is comparable to Al$_2$O$_3$ in preventing catalyst particle sintering, so promoting mat growth. This study suggests that CoSi2 is a promising candidate as a conductive support layer for growth of horizontal CNT interconnects. Further experiment is being carried out to fabricate these devices.

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