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THE EFFECT OF TITANIUM NITRIDE THICKNESS AS A SUPPORT LAYER FOR CARBON NANOTUBES GROWTH

The effect of titanium nitride (TiN) thickness as the support layer for carbon nanotubes (CNTs) growth was investigated by depositing three different thicknesses: 20 nm, 50 nm and 100 nm. This TiN support layer was deposited on SiO_2 pads before depositing nickel (Ni) as the catalyst material. The Ni distribution on different TiN thicknesses was studied under hydrogen environment at 600°C. Then, the samples were further annealed at 600°C in acetylene and hydrogen environment for CNTs growth. The results show that, the optimum TiN thickness was obtained for 50 nm attributed by the lowest D to G ratio (0.8).

Keywords: Titanium Nitride; Support Layer; Carbon Nanotubes; Interconnection

1. Introduction

Generally, aluminum (Al) and copper (Cu) are the most common materials used in interconnection for CMOS devices. The typical current density that can be generally achieved by Al and Cu are around 10^6 to 10^8 A/cm^2 respectively [1]. However, it will fail because of electro migration problem occurred [2]. Thus, an alternative material needs to be proposed. Due to the extraordinary properties in structural, electrical and mechanical, this carbon-based material becomes the promising and relevant solution to this problem as the common materials start to fail [3,4]. The most critical part for CNTs based interconnect is to grow the nanotubes on metal contact [5]. Metals like Nickel (Ni), Ferum (Fe) and Cobalt (Co) are the materials that usually used as the catalyst [6]. When these catalysts were exposed at certain hydrocarbon gas under a controllable environment of time, pressure and temperature, it will initiate the growth of CNTs which further affected by some other factors like metal support layer [7-9]. Thin film metal can be deposited on top of the Si/SiO_2 substrate which serve as the diffusion barrier layer to the interconnect [10]. This layer can facilitate the nanotubes growth by preventing the diffusion of catalyst material and resulting low contact resistance interconnect [11].

Stated thus, many materials were investigated as the support layer. Previously, Al and Aluminum Nitride (AlN) [12,13] were dominated and investigated due to the good conduction and adhesion. However, these materials were not stable at high temperature and suffer with oxidation issue. Then, Titanium (Ti) was applied but the same oxidation problem occurred. Besides, there is a claim that CNTs only grow on low surface energy material (0.8-1.2 Jm^{-2}) such as Platinum Silicone (PtSi) [14]. The ultimate aim of this study is to successfully grow CNTs on high surface energy material (1.4-1.6 Jm^{-2}), which is Titanium Nitride (TiN). TiN was proposed as the support layer for interconnect based on its excellent diffusion barrier layer properties, good electrical conductivity, stable at elevated temperature and high corrosion resistance. In this report, the effect of TiN thickness as the support layer for CNTs based interconnect was studied and investigated.

2. Experimental details

Pads in the size of 3 × 3 mm^2 were prepared on SiO_2 substrate. Different thickness of 20 nm, 50 nm and 100 nm TiN [10] was deposited by sputtering using Single Wafer Sputter Deposition Processing System (MPS 500 Series from JLS Design) at 0.2 A with the ratio of 16:10 Ar and N_2 environment for 20 minutes, 50 minutes and 100 minutes. The uniform yellowish thin film was obtained in different ranges indicated as the evidence of

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TiN at different thickness which confirmed by the profilometer, Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). The required pads were continuously prepared using photolithography process. In order to observe the growth of CNTs, 5 nm nickel (Ni) catalyst were deposited using the same sputtering technique at 0.14 A for 2 minutes. The unwanted metal catalyst was removed by lift-off process. Then, these samples were annealed in thermal chemical vapour deposition cold wall chamber under H_2 environment for 15 minutes at 600°C in order to observe the catalyst evolution on TiN layer. For CNTs growth, the same annealing process was done at 600°C in C_2H_2 and H_2 environment (flow rates of 4:100 sccm) and process pressure of 2 Torr for 15 minutes using the same chamber. The density and quality of CNTs were characterized using SEM and Raman Spectroscopy. Catalyst distribution on TiN support layer has been analyzed using ImageJ software.

3. Results

TiN was very stable at high temperature (melting temperature 2,930°C) which implies that this material will not easily react and mix with the catalyst material during annealing process [10]. The grain size of TiN was confirmed very similar before and after annealed at 600°C with very low surface roughness, uniformly textured and without recrystallization. It was also very stable after deposited with 5 nm Ni thin film as shown in Fig. 1. However, small variations on the surface roughness were identified across different TiN thicknesses. From SEM inspection, the surface morphology of TiN when annealed at the growth temperature of 600°C does not show any visible differences across the TiN thicknesses. It was believed that the thin film support layer can initiate the catalyst film breaks much into islands and aggregate to form bigger particles due to its higher surface tension, its interfacial energies with the catalyst particle and volume that affect the contact angles between them (catalyst-support layer).

TABLE 1

Surface roughness of different TiN thickness

TiN Thickness	Root Mean Square Roughness
20 nm	0.3 nm
50 nm	0.5 nm
100 nm	0.6 nm

A 5 nm Ni thin layer was deposited, as the catalyst film, on top of TiN support layer. When the heat applied, the Ni thin film will break into islands and some of them will coalesce and aggregate which follows the theory of Volmer-Webber [15]. The catalyst distribution on different thickness of TiN was investigated at the same process temperature, 600°C. At different thicknesses, the distributions of Ni were quite similar compared to the distribution of Ni affected by different process temperature and deposition method which were demonstrated in the previous work [16]. It has been reported that, going to higher temperature the particles count was decreased but the average diameter was increased due to particle coalesced [16]. Ni evolution of 50 nm TiN that was annealed at 600°C with particle average of 55.8 nm is shown in Fig. 2.

The effect of TiN thickness on CNTs was studied and presented in Fig. 3 (a-c). At 20 nm TiN, bundles of small CNTs with no preferential direction were obtained. As the thickness increased up to 50 nm, the length of CNTs is increased and the nanotubes were getting thicker. However, at 100 nm TiN, the density of CNT is extended but size of the nanotubes was decreased. These bundles of nanotubes which resulted for all TiN thicknesses might happen because of some factors such as the presence of pre-treatment process in H_2 that led to the removal of the native oxide and deposition method of the support layer. According to Esconjauregui [17], partial reduction of the oxides which can happen during the oxidation of the catalyst even at room temperature was needed to stabilize the catalyst particles and prevent it from diffusion into the bulk, especially for the growth process on high surface energy material. Besides, the deposition method of TiN with other method such as atomic layer deposition (ALD) rather than sputtering will give better control and high yield growth of CNTs [18].

The quality of these growths was characterized using Raman Spectroscopy as shown in Fig. 4. From the Raman spectra, typical multi-walled CNTs (MWCNTs) peaks were observed

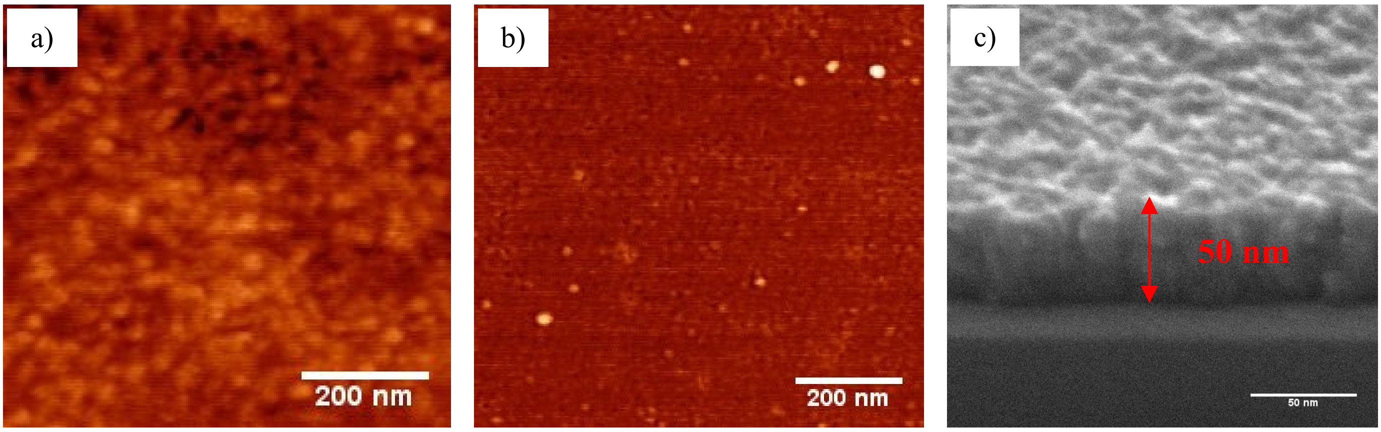

Fig. 1. AFM images of 50 nm TiN (a) without Ni catalyst, (b) with 5 nm Ni catalyst and (c) SEM cross section of 50 nm TiN on SiO_2

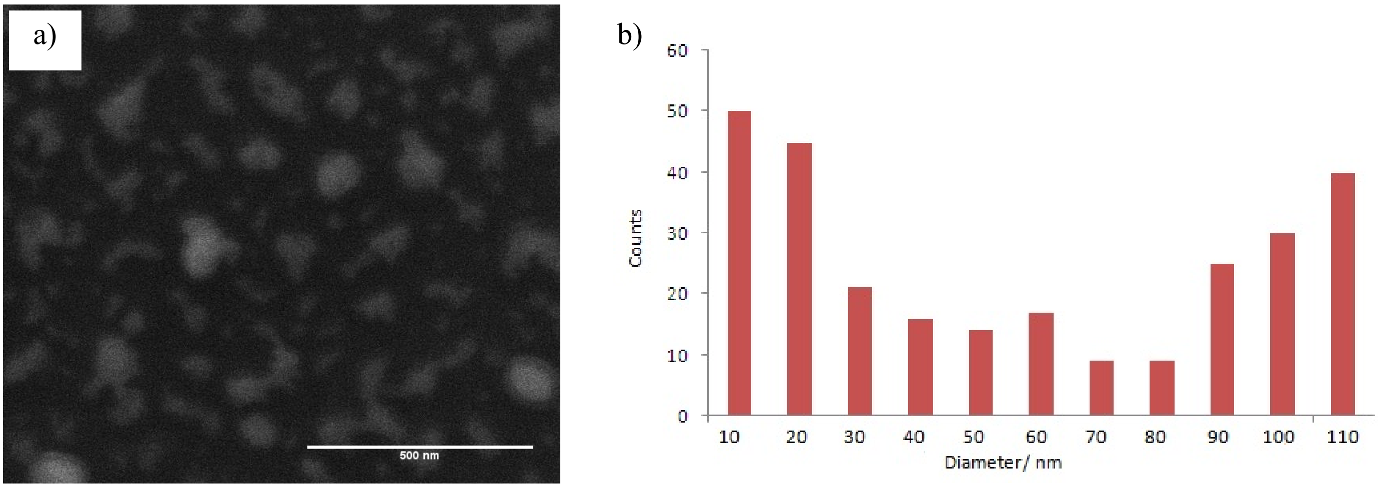

Fig. 2. Ni (5 nm) distribution on 50 nm TiN annealed at 600°C (a) SEM image and (b) particle plots

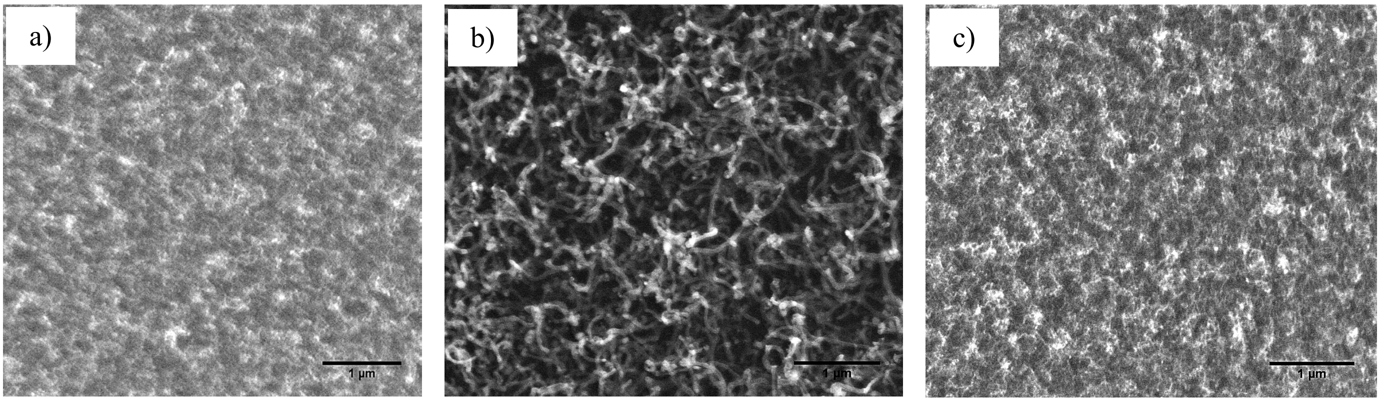

Fig. 3. SEM images of CNTs on TiN (a-c) 20 nm, 50 nm and 100 nm

at G band (1590 cm^{-1}) and D band (1350 cm^{-1}). At 20 nm, the intensity of D and G peak was very low resulted by the sparse growth as the strong Si peak was observed at 514 cm^{-1}. 50 nm of TiN thickness seems to be the optimum thickness for CNTs growth when the D to G ratio shows the lowest. For 100 nm TiN, although the high density of CNTs was observed, the defect at this condition was very high represented by the D peak and highest D/G ratio.

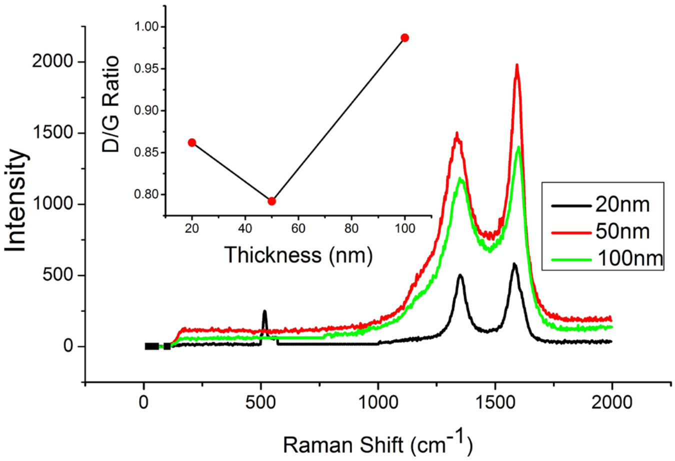

Fig. 4. Raman spectra of MWCNTs at different TiN thickness

4. Summary

In order to investigate the effect of TiN thickness as the support layer on CNTs growth, three thicknesses (20, 50 and 100 nm) were deposited. From this study, it shows that TiN was a stable material as the support layer at high process temperature. Very low surface roughness indicates the uniform deposition film was obtained for all deposited thicknesses. The different thicknesses do not show any clear effect on the catalyst distribution at 600°C process temperature. For CNTs growth, 50 nm of TiN becomes the optimum thickness as high density and quality CNTs was attained.

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