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Temperature-dependent selective growth of carbon nanotubes in Si/SiO_2 structures for field emitter array applications

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ABSTRACT

Temperature-dependent selective growth of Carbon Nanotubes (CNTs) in Si/SiO_2 structures using ferrocene/xylene volatile catalyst source and its application in Field Emitter Array (FEA) is demonstrated in this work. CNTs are grown directly on Si/SiO_2 substrates by volatile catalyst source (Ferrocene/Xylene) Chemical Vapor Deposition (CVD) technique and the effect of growth temperatures (760–880 °C) on CNT height and crystallinity has been studied. Selective growth of CNTs on Si substrates is achieved at 790 °C growth temperature. Using the obtained selective growth condition, CNT FEAs are fabricated by growing CNT bundles selectively on the Si surface of the pre-fabricated SiO_2 pits on a Si wafer. Field emission current density above 100 mA/cm^2 is obtained from inter-pit separation distances of 4–10 μm. These results show the potential of ferrocene/xylene catalyst source in achieving selective growth of CNTs in Si/SiO_2 structures for FEA application.

1. Introduction

As predicted by Moore's law, there has been an exponential increase in the number of components fabricated on a commercial semiconductor chip over the past few decades [1]. Along with this progression, several technical issues have arisen, including off-leakage increase and drain current degradation [2]. To resolve these technical issues, it has been proposed by NASA to use vacuum electronic devices as a possibly better alternative as compared to the conventional Silicon (Si)-based solid-state electronic devices [3]. In general, vacuum electronic devices possess higher electron mobility, thermal durability and wider operational frequency range as compared to solid-state devices. However, vacuum electronic devices are heavier and bulkier than solid-state devices, which limits their applications in modern electronic systems [4]. In the proposal made by NASA, a possible strategy to miniaturize vacuum electronic devices has also been suggested, which includes integration of Si based microfabrication techniques in the fabrication process of vacuum electronic devices [3].

To enable the microfabrication of vacuum electronic devices, miniaturized, high current density field emitters with high growth selectivity are required. Various 1D nanostructure field emitters have been reported in the state-of-the-art, such as diamond nanowire [5], ZnO nanowire [6], silver nanowire [7], Carbon Nanotubes (CNTs) [8] *etc.* These nanostructures show promising Field Emission (FE) characteristics for possible application in modern vacuum electronic devices. Among the reported nanostructures, Carbon Nanotubes (CNTs) show outstanding FE properties resulting from their unique atomic structure [8]. A typical CNT Field Emitter Array (FEA) can be fabricated on a pre-deposited catalyst pattern (Ni, Fe, Co, *etc.*) via Chemical Vapour Deposition (CVD) technique [9]. By using this technique, CNTs can be grown selectively on the pre-patterned catalyst layer. Besides pre-patterned catalyst technique, a simpler approach to fabricate CNT FEA is the *in-situ* volatile catalyst source (ferrocene/xylene) CVD technique [10]. Due to the organometallic (Fe-hydrocarbon) nature of ferrocene, the Fe content in ferrocene can act as a catalyst for CNT growth without the presence of an external catalyst layer. Zhang et al. [11] have reported CNT growth on pristine Si substrates using volatile catalyst source technique. From the reported study, CNT growth is initiated by the formation of a continuous iron silicide barrier layer on the silicon substrate; the iron silicide is postulated to reduce the contact resistance between CNTs and the Si substrate. In addition to growth of CNTs using ferrocene/xylene catalyst, to successfully integrate ferrocene-grown CNTs in FEA

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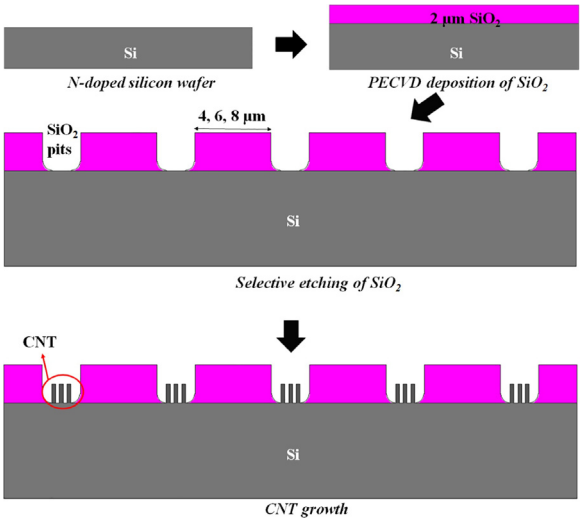

Fig. 1. Schematic diagram of CNTs grown in Si/SiO_2 structure.

applications, selective growth of CNTs in Si/SiO_2 structures is crucial. Jung et al. have reported selective growth of CNTs in Si/SiO_2 structures on the SiO_2 surfaces using volatile catalyst technique. From the suggested mechanism, high selectivity of CNT growth is achieved when a continuous layer of γ-Fe is formed on the SiO_2 layer and large clusters of $FeSi_2$ or $FeSiO_4$ are formed on the silicon surface [12]. However, a significant drawback of this technique is the high resistivity of SiO_2 layer [13], which will increase the electrical contact resistance between CNTs and Si substrate and limit its performance.

In order to achieve selective growth of CNTs on the Si surface, Labunov et al. have reported the reversible selective growth of CNTs on either Si or SiO_2 surfaces by varying the gas dynamic factors in a CVD process. In the reported outcomes, reversible selective growth of CNTs has been achieved on either Si surface or 100 nm thick SiO_2 surface, depending on the gas flow rate [14]. Besides gas dynamic factors, an important factor in determining the selectivity of CNT growth on Si/SiO_2 substrates is the growth temperature. As the selectivity of CNT growth on Si/SiO_2 substrates relies heavily on the thermo-diffusivity profile of Fe particles on the Si/SiO_2 substrates, growth temperature significantly impacts the selectivity of CNT growth [12]. In the investigations on the temperature-dependent growth of CNTs by volatile catalyst (ferrocene/xylene) source CVD technique, Sengupta et al. have reported improvements in the crystallinity of CNTs at higher synthesis temperatures [15]. At the same time, Bai et al. have reported temperature-dependent profile of CNT growth rate by changing the pyrolysis temperature in the CNT synthesis process [16]. Besides the temperature-dependent profile, Kar et al. have investigated the effect of substrate heating and microwave attenuation on the field emission properties of ferrocene-grown CNTs. From the reported work, substrate heating and microwave attenuation contribute to drastic improvement of CNT field emission current density from 200 $\mu A/cm^2$ to 14.5 mA/cm^2 [17]. Nevertheless, to realize the integration of the nanostructured field emitter in modern vacuum electronic applications, a clearer understanding of the mechanism in the temperature-dependent selective growth of CNTs on Si/SiO_2 structures is required. But there exist only limited studies on this issue. Therefore, studies on the temperature-dependent growth of CNTs on Si/SiO_2 substrates are called for.

In this study, we first perform a comparative study on the temperature-dependence of CNT growth on pristine and 2 μm SiO_2-deposited Si substrates. Selective growth of CNTs on pristine Si substrate at 790 °C is achieved. The possible mechanism of the selective growth condition is discussed. By utilizing the achieved selective growth condition, we fabricate CNT FEAs by growing CNT bundles selectively at the Si surface in fabricated SiO_2 pits at inter-pit separation distances of 4–10 μm. Field emission current density greater than 100 mA/cm^2 is obtained for all inter-pit distances. The effect of inter-pit distance on the FE properties of CNT FEAs is also explored by electrostatic simulations which further explain the experimental observations.

2. Experimental method

Carbon Nanotubes (CNTs) are grown on 2 μm SiO_2-deposited and pristine Si substrate using Chemical Vapour Deposition (CVD) with a volatile catalyst source as reported by Navitski et al. [18]. A typical CVD process is carried out in a quartz tube reactor through

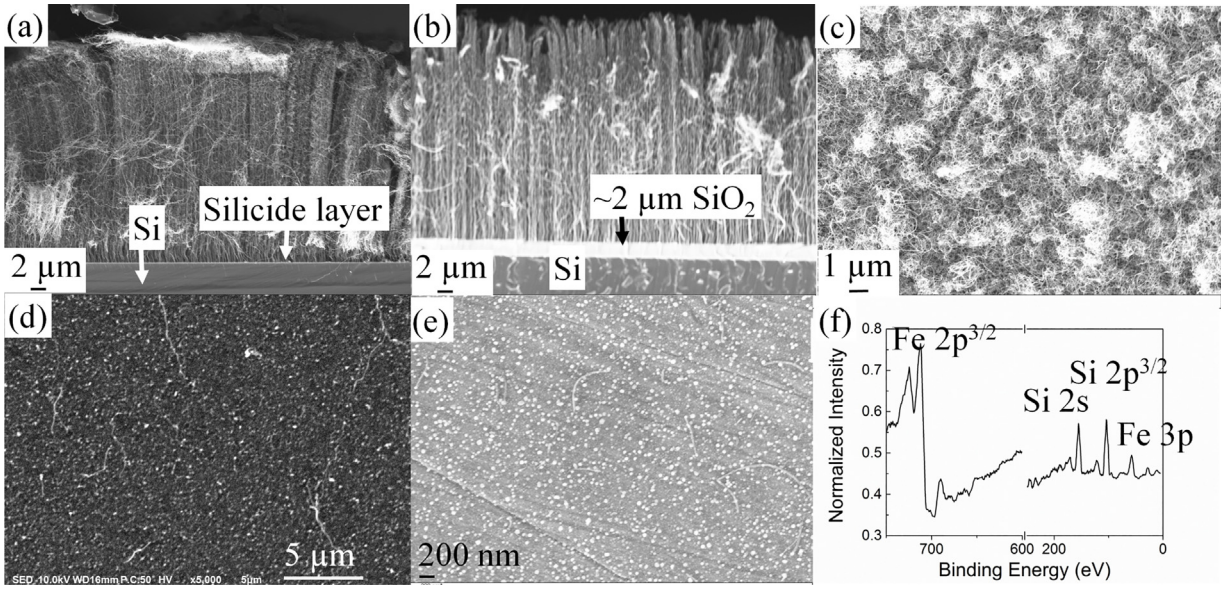

Fig. 2. SEM images: Cross sectional view of CNTs grown on (a) Si and (b) SiO_2 substrates at 860 °C growth temperature; plan view of CNTs grown on Si substrates at (c) 790 °C and (d) 860 °C growth temperatures. (e) SEM image and (f) XPS Spectra of $FeSi_2$.