

## GROWTH OF CARBON NANOTUBE BY APPLYING ION IMPLANTATION TECHNIQUE

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### ABSTRACT

#### GROWTH OF CARBON NANOTUBE BY APPLYING ION IMPLANTATION TECHNIQUE.

The use of ion implantation technique for growing carbon nanotubes (CNT) has been studied. Implantation technique with its high and focused energy is used for implanting Ni<sup>+</sup> ion, which can act as catalyst for CNT growth. CNT was grown by implantation of Ar<sup>+</sup> and Ni<sup>+</sup> ion to the nanostructured carbon thin film that were deposited on Si(100) substrate. The dose of ion implantation parameter was varied between  $5 \times 10^{15}$  to  $1 \times 10^{17}$  ion/cm<sup>2</sup>. After implantation, the phase identification by X-Ray diffraction (XRD) and observations of surface and cross section morphology of samples by Scanning Electron Microscopy (SEM) in order to investigate the growth of CNT were carried out. The XRD analysis shows the peak of C(002), Ni(010) and Si(100) on the C/Si thin film samples after ion implantation, which indicate the carbon film still in a crystalline structure. The peak of Ni(010) is slightly decreased with the increasing of ion dose. The observation by SEM shows that the greater the dose of implants, the more unflat surface found on a thin film. While from the observation of cross section, it was indicated that the higher dose implants, more clearly the growth of CNTs on the surface of C/Si thin film. CNT is predicted to grow as a result of interaction between ion radiations with carbon, leading to the formation of CNTs.

**Keywords:** Thin Film, CNT, Ion Implantation Technique, Dose

### ABSTRAK

**PERTUMBUHAN CARBON NANOTUBE DENGAN TEKNIK IMPLANTASI ION.** Pemanfaatan teknik ion implantasi untuk menumbuhkan *Carbon Nanotube (CNT)* telah dilakukan. Teknik implantasi dengan energi yang tinggi dan terfokus digunakan untuk mengimplantasi ion Ni<sup>+</sup>, dimana ion ini dapat berfungsi sebagai katalis untuk pertumbuhan *CNT*. *CNT* ditumbuhkan dengan mengimplantasi ion Ar<sup>+</sup> dan Ni<sup>+</sup> ke dalam lapisan tipis karbon berstruktur nano yang dideposisikan di atas substrat Si(100). Dosis parameter implantasi ion divariasikan mulai dari  $5 \times 10^{15}$  ion/cm<sup>2</sup> hingga  $1 \times 10^{17}$  ion/cm<sup>2</sup>. Setelah implantasi, dilakukan identifikasi fasa dengan *X-Ray Diffraction (XRD)* dan dilakukan observasi morfologi permukaan dan penampang melintang dengan *Scanning Electron Microscope (SEM)* dalam rangka untuk mengetahui kondisi pertumbuhan *CNT*. Analisis *XRD* memperlihatkan adanya puncak C(002), Ni(010) dan Si(100) pada sampel lapisan tipis C/Si setelah implantasi ion, dimana mengindikasikan lapisan tipis karbon masih memiliki struktur kristal. Intensitas puncak Ni(010) sedikit mengalami penurunan seiring dengan peningkatan dosis ion. Hasil observasi dengan *SEM* menunjukkan bahwa semakin besar dosis *implant*, permukaan lapisan tipis akan semakin tidak merata. Sedangkan dari observasi penampang melintang, dapat diindikasikan bahwa semakin tinggi dosis *implant*, pertumbuhan *CNT* di atas permukaan lapisan tipis C/Si menjadi semakin jelas. *CNT* diprediksi tumbuh sebagai hasil dari interaksi antara radiasi ion dengan karbon, yang mengarah kepada pembentukan *CNT*.

**Kata kunci:** Film tipis, *CNT*, Teknik Implantasi Ion, Dosis

### INTRODUCTION

Owing to their unique structure and properties, carbon nanotubes (CNTs) have attracted considerable attention the last decade since their discovery in 1991 [1]. There are two general categories of nanotubes. One is represented by single-walled nanotubes (SWNT) that consist of a honeycomb network of carbon atoms, and

can be imagined as a cylinder rolled from a graphitic sheet. The other is multi-walled nanotubes (MWNTs) that is a coaxial assembly of graphitic cylinders generally separated by the plane space of graphite [2]. This makes nanotubes challenging materials with special characteristic of atomic structure and physical properties,

and therefore the nanotubes become the most promising candidate for building blocks of molecular-scale machines and nanoelectronic devices [2-7]. Furthermore, there are many potential applications of carbon nanotubes, such as catalyst supports in heterogeneous catalysis, components of composites, high-strength fibers, and sensors, result mainly from high surface area, mechanical strength, chemical and thermal stability of carbon nanotubes [8].

Currently, several techniques, such as electric arc-discharge, laser evaporation/ablation and chemical vapor deposition (CVD), catalytic chemical vapor deposition (CCVD) through the decomposition of hydrocarbon have been successfully developed to synthesize CNT. The CVD and especially the CCVD method requires a lower reaction temperature with the potential for a low cost of production. These methods are the best possibility for large-scale production, and the CCVD method has been successfully used to produce aligned carbon nanotubes [9] and single-walled carbon nanotubes (SWNTs) [10]. In the case for research usage, the suitable methods for producing CNT are the first two methods that can produce high-quality nanotubes [11,12]. Nanotubes are usually grown on nanoparticles of magnetic metal (Fe, Co and other metal), which facilitates production of electronic (spintronic) devices.

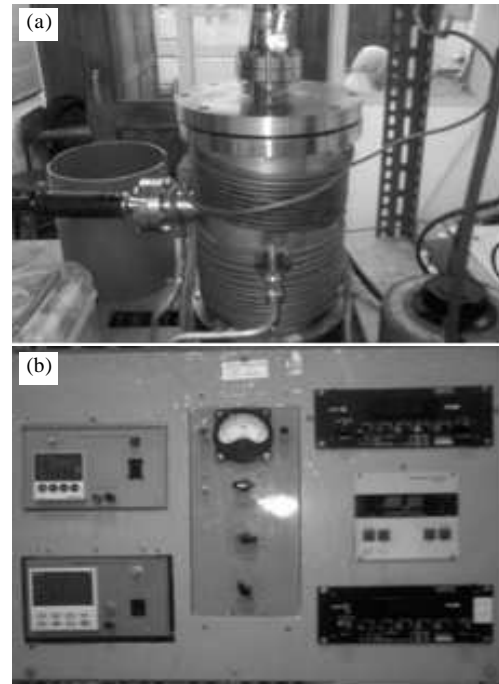
In this paper we present the study on the growing of CNT by using ion implantation technique, after preparing of carbon thin film by DC-Sputtering method used nanostructured carbon pellet, that is composed of nanosize of carbon powder prepared by High Energy Milling (HEM).

## EXPERIMENTAL METHODS

Carbon material used as a target of DC-Sputtering for producing carbon thin film on Si(100) substrate is nano structured carbon in the form of pellet, which are composed of carbon powder prepared by milling process for 50 hours. A formed carbon pellet has the dimension of 25 mm in diameter with a thickness of 5 mm. A press machine was used to prepare carbon pellet, which the press machine is a hydraulic type, brand of Daiwa Universal Testing Machine, with the following specifications: rat 100, capacity 100 tons, a power source

**Table 1.** Setting parameter of DC-Sputtering and other information at the time of producing carbon thin film.

Parameter	Value / Remark	Unit
Substrate	Si(100)	-
Target	Carbon	-
Distance between substrate-target	400	mm
Temperature of substrate	573	K
Current	0.033	A
Voltage	600	V



**Figure 1.** The photograph of chamber and control device in the sputtering equipment used in this study: (a). The Chamber of Sputtering Equipment and (b). The Control Device of Sputtering Equipment.

voltage is 220 VAC, made by Daiwa Kenko, Co. Ltd. From our previous research, it was obtained that the milling process can be used to crush the size of carbon powder until nano size. Nano sized powder was then used to make sputtering target, in order to get nano structured thin film as well. More detailed information about the preparation of nano sized powder and nano-sized morphology of thin film can be found in our previous reports [13,14]. The graphite powder used for preparing carbon target is graphite powder (Carbon, C) from Aldrich product with the purity of 99.5 %. The parameters of DC Sputtering for producing carbon thin film are 573 K of deposition temperature and 180 minutes of deposition time (sputtering time). The other parameter settings for producing carbon thin film are written in the Table 1, while Figure 1 shows the chamber part (a) and control panel part (b) on the DC Sputtering equipment.

After carbon thin film is formed, the implantation process using  $\text{Ni}^+$  ion and  $\text{Ar}^+$  ion to the nano structured carbon thin film was carried out by using ion implantation equipment. The implantation process here was conducted with the aim of an effort to grow the carbon nano tube on the surface of the carbon thin film. The ion implantation process using  $\text{Ni}^+$  ion and  $\text{Ar}^+$  ion was applied to the carbon thin film as a technique for growing carbon nanotubes (CNTs). Nickel ions of energy in 70 keV were first implanted into the carbon thin film, then next Argon ion were implanted, which both were at room temperature. The parameters used here is implantation dose, and the dose of  $\text{Ni}^+$  ion and  $\text{Ar}^+$  ion

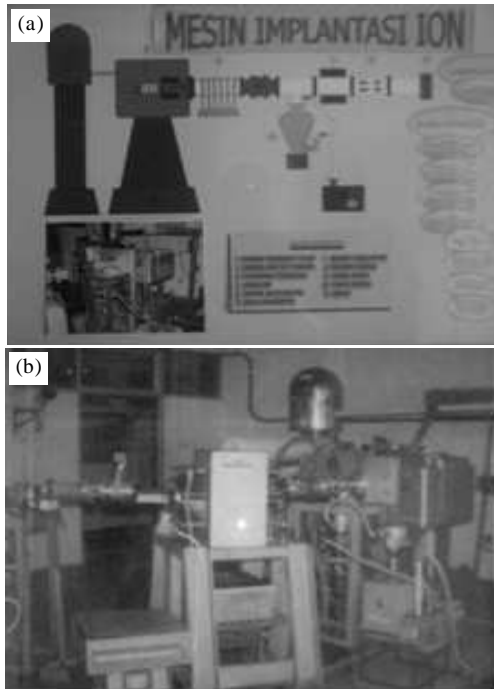


Figure 2. The photograph of ion implantation facility used in this research : (a). The Scheme of Ion Implantation Equipment and (b). The Figure of Ion Implantation Equipment.

was varied from  $5 \times 10^{15}$  ions/cm<sup>2</sup> to  $1 \times 10^{17}$  ions/cm<sup>2</sup>. The other parameters of implantation process are 70 keV of doping energy, 20 mA of current,  $10^{-5}$  mbar of vacuum level,  $1.603 \times 10^{-19}$  of Ar electron charge, and 12.566 cm<sup>2</sup> of the cross sectional area of ion beam source. The equipment of ion implantation used in this study is showed in Figure 2. The ion source of Ni<sup>+</sup> is Ni powder, while for Ar<sup>+</sup> is Ar gas.

The crystal structure was analysed by X-Ray Diffraction (XRD) taken with a Phillips APD 3520 Diffractometer, using Cu radiation. The morphology and cross-sectional of carbon thin film before and after implantation process were observed by JEOL-Scanning Electron Microscopy (SEM).

## RESULTS AND DISCUSSION

### Carbon Thin Film Before Process of Ion Implantation

The crystal structure was analysed by X-Ray Diffraction spectroscopy using a Cu K<sub>α</sub> source. The results obtained from a carbon thin film sample are reported in Figure 3. With regard to carbon (C), the pattern shows a small peak from C (002), which indicate that the carbon film is crystalline structure. The graphite structure is still dominant, dominated by the hexagonal phase (JCPDS No. 41-1487), because other diffraction peak of C was not identified. Moreover, the peak from Si(100) is detected and very sharp, indicating the direction of the Si(100) substrate used in

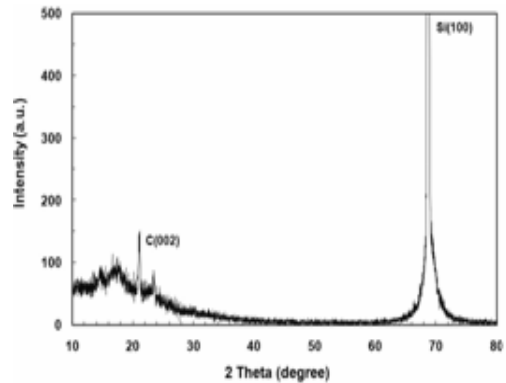


Figure 3. XRD carbon thin film before ion implanting.

this study. The interlayer spacing  $d_{002}$  was determined from the 002 peak by applying Bragg's law with a wavelength of  $\lambda = 0.1003$  nm. It was found to be 0.342 nm for carbon thin film sample, which is slightly larger than that of bulk graphite (0.335 nm).

Figure 4 shows top view and cross sectional of SEM images of carbon thin film grown on Si(100) substrate for 180 minutes at the sputtering temperature of 573 K by using DC Sputtering. Top view of SEM image is used to determine the homogeneity of the carbon thin film. It is needed to know the homogeneity level of the thin film, which the homogeneity plays a very crucial role, especially to explore the possibility of the formation of CNTs on the surface of thin film. From Figure 4 that shows the top view image (surface morphology) of carbon thin film (Figure 4 (a)), a smooth condition of thin film was generated, and from the result of EDX it is clearly shown

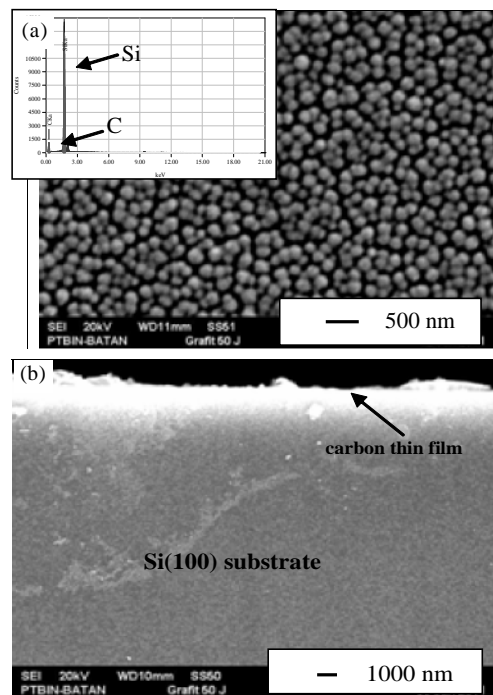


Figure 4. SEM photograph and EDX analysis result of carbon thin film deposited on Si(100) using DC Sputtering.

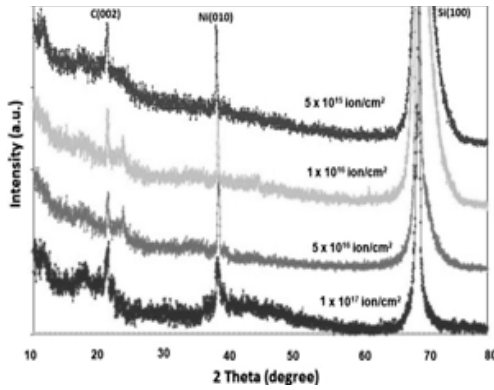


Figure 5. XRD pattern of carbon thin film after ion implanting.

that the carbon particles have been deposited on the surface of the Si(100) substrate, which is shown by gray color of a circle object that is dispersed on the surface of the Si(100) substrate. The carbon nanoparticles are visible in the top view image. A cross-sectional image is taken to know the thickness of thin film as seen in Figure 4 (b). The carbon thin film deposited on the Si(100) substrate has a thickness of approximately around 800 nm.

### Carbon Thin Film After Process of Ion Implantation

Figure 5 shows the XRD pattern of carbon thin films that have been implanted by Ni<sup>+</sup> ion and Ar<sup>+</sup> ion. Overall the peak of C(002), Ni(010) and a very dominant of Si(100) peak were detected. At the angle of 68.74° the peak appears that is identified as a peak of Si(100) substrate of thin film. The peak that is identified as the peak of C(002) and Ni(010) appears at the angle of 21.52° and 39.48°. The numbers written on the Figure 5 imply the amount of dose at the time of ion implantation process performed.

From the results of XRD analysis, no significant differences were found either in intensity or in peak angle shift with increasing dose of ion implants. The changes are only in the peak of Ni(010), which the intensity is slightly decreased with the increasing of ion doses. The energy used in the process of ion implantation is relatively small that is around 70 keV, so that the slightly decreasing of Ni peak's intensity along with the increasing of doses was happened because the previously implanted atom (the ion that previously implanted in the surface of carbon thin film) were sputtered by the incoming Ni<sup>+</sup> ion. When the fluence is increased, the concentration of implanted element saturates. It is need to increase the energy of implantation process, in order to overcome problem of sputtering of implanted atoms.

Nevertheless, the appearance of peak of Ni from the XRD pattern result is an evidence of the occurrence the formation of Ni catalytic nano particles at the surface

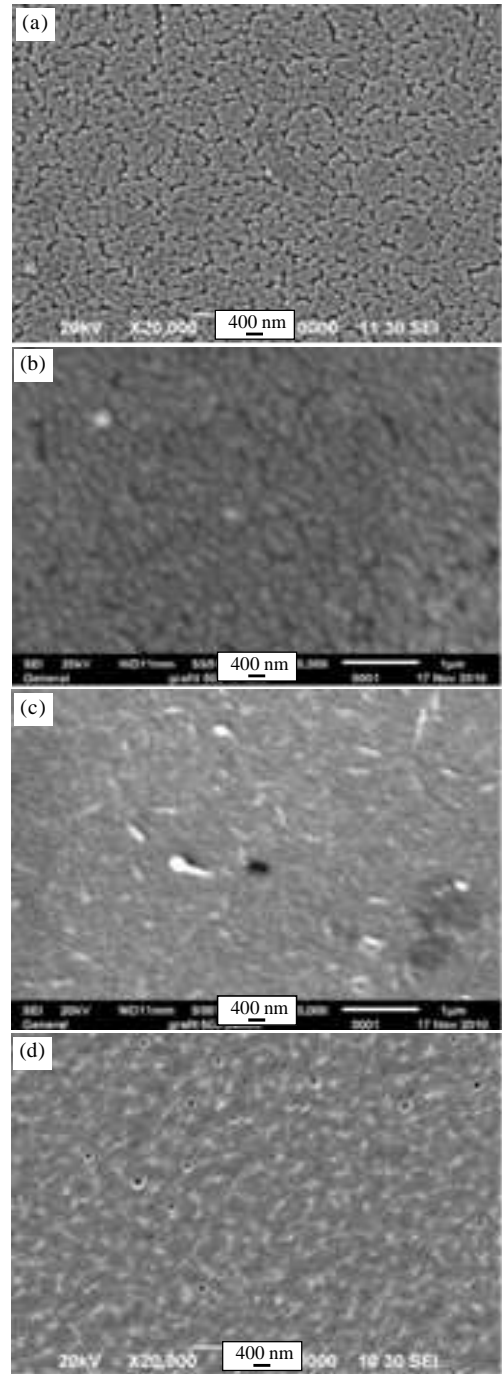
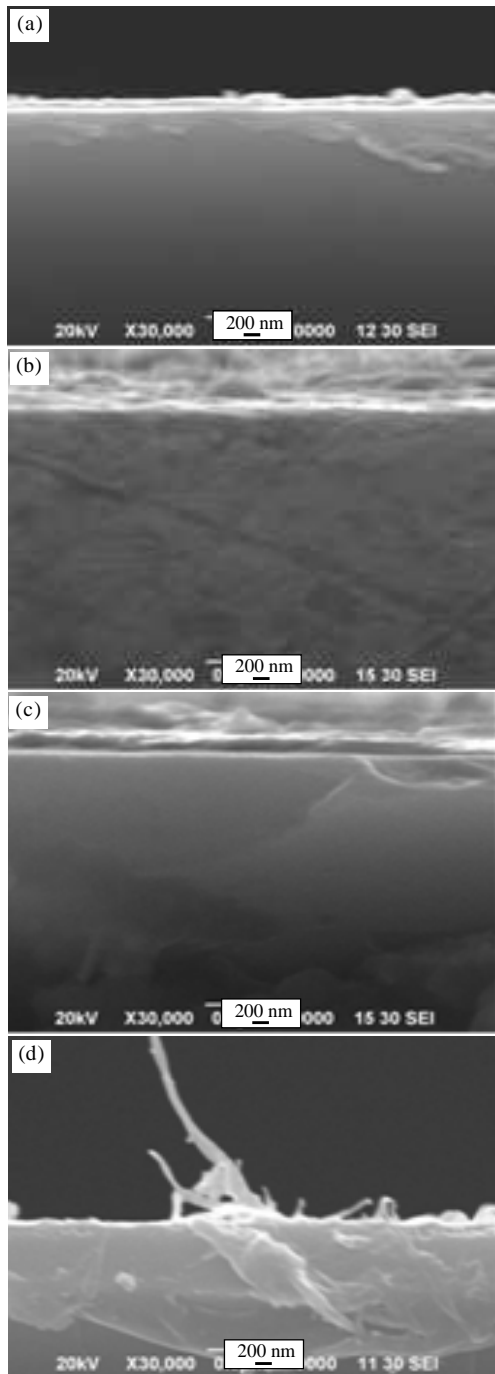


Figure 6. Surface image of carbon thin film after ion implanting using Ni<sup>+</sup> followed by Ar<sup>+</sup> with energy of 70 keV at room temperature : (a). 5 x 10<sup>15</sup> ion/cm<sup>2</sup>, (b). 1 x 10<sup>16</sup> ion/cm<sup>2</sup>, (c). 5 x 10<sup>16</sup> ion/cm<sup>2</sup> and (d). 1 x 10<sup>17</sup> ion/cm<sup>2</sup>.

of carbon thin film. These Ni catalytic nano particles will be used as an initial of growing CNT.

Figure 6 shows the top view (surface) of carbon thin films that have been implanted by Ni<sup>+</sup> ion and Ar<sup>+</sup> ion with (a). 5 x 10<sup>15</sup>, (b). 1 x 10<sup>16</sup>, (c). 5 x 10<sup>16</sup> and (d). 1 x 10<sup>17</sup> ion/cm<sup>2</sup> of 70 keV, which the image was observed by SEM. The size of the formed clusters is quite uniform in all doses ion, but the amount of clusters decreases with the increasing of doses ion.



**Figure 7.** Cross-sectional image of carbon thin film after ion implanting using Ni<sup>+</sup> followed by Ar<sup>+</sup> with energy of 70 keV at room temperature : (a).  $5 \times 10^{15}$  ion/cm<sup>2</sup>, (b).  $1 \times 10^{16}$  ion/cm<sup>2</sup>, (c).  $5 \times 10^{16}$  ion/cm<sup>2</sup> and (d).  $1 \times 10^{17}$  ion/cm<sup>2</sup>.

From the top view (surface) of SEM observation, the formation of CNT cannot be observed on the carbon thin film surface.

Next, to know the embryo of CNT formation is also used SEM by shooting a sample from cross direction or cross-sectional observing. As shown in Figure 7, pieces of long fiber assumed as the embryo of CNT formation is observed on the top surface of the carbon thin film, especially in the case of ion implantation

$1 \times 10^{17}$  ion/cm<sup>2</sup> of dose. It is clear that nanotubes were randomly growth on the surface of the carbon thin film. The nanotubes have an average diameter of 20-40 nm, and some of them cross each other. CNT is growing with the definite and clear in the top surface of carbon thin film, along with the increasing of ion implant dose. This means that the bigger of dose is implanted, the higher of the formation of Ni nano particle on the surface of carbon thin film, which in turn will encourage more and more CNT grown on the surface of carbon thin film. As written above, the main target of implanting Ni<sup>+</sup> ion is to use Ni as a catalyst for growing CNT. From this experiment also proved the role of Ni as a catalyst for growing CNTs, where the CNTs grown with the obvious and best when the process of implantation was carried at the largest dose ( $1 \times 10^{17}$  ion/cm<sup>2</sup>). To know the structure of CNT needs to be clarified by using TEM observation and this will be the subject of research in the future.

## CONCLUSION

Based on this research, it can be concluded that the application of Ni<sup>+</sup> followed by Ar<sup>+</sup> ion implantation can be used to synthesize CNT with an average diameter of 20-40 nm at the surface. The ion implantation with a small energy of keV ions are useful for obtaining nano particle and CNT in the top of carbon thin film. Ni indicates an important role in the growth of CNTs, which means that Ni successfully grown on carbon thin films as catalysts for CNT growing.

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