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GROWTH OF CARBON NANOTUBE FROM NANOSTRUCTURED COMPOSITE OF Fe-C USING ION IMPLANTATION TECHNIQUE

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ABSTRACT

GROWTH OF CARBON NANOTUBE FROM NANOSTRUCTURED COMPOSITE OF Fe-C USING ION IMPLANTATION TECHNIQUE. Growth of carbon nanotube (CNT) from nanostructured composite of Fe-C has been carried out using ion implantation technique. The CNT developed here is expected to be used as an Integrated Sensor System, because CNT offer promises for future nano-electronic sensor applications, and reliably controlling CNT growth has been a big challenge. Nanostructured composite of Fe-C was prepared by milling for 50 hours. The size of Fe-C powder was determined from Scanning Electron Microscope (SEM) image. Milled powder then was compressed to get pellet form of Fe-C, and used as a target in fabricating thin film of Fe-C on Si(100) substrate using sputtering technique. Further, the ion implantation was done against the Fe-C thin film. The ion source using Argon gas, in order to make growth of CNT until the densitiy dose of 5 x 10^{15} ions/cm^2. The phase of formed CNT was identified by X-Ray Diffractometer (XRD), the morphology of surface was observed by SEM. From this research, it has been showed that the milled composite of Fe-C has a powder size until nano order size. From XRD data, it is identified that only Fe and C peaks were confirmed. On the other hand, the observation on the surface of Fe-C thin film showed the growth of CNT.

Key words **:** Carbon Nanotube, Integrated Sensor System, Composite of Fe-C, Ion Implantation

ABSTRAK

PENUMBUHAN *CARBON NANOTUBE* DARI KOMPOSIT Fe-C STRUKTUR NANO DENGAN TEKNIK IMPLANTASI ION. Telah dilakukan penelitian penumbuhan *carbon nanotube* (*CNT*) dari komposit Fe-C struktur nano dengan teknik implantasi ion. Komposit Fe-C struktur nano dibuat dengan metode *milling* selama 50 jam. Setelah itu, ukuran serbuk Fe-C ditentukan dari hasil pengamatan dengan *Scanning Electron Microscope* (*SEM*). Serbuk hasil *milling* dibuat dalam bentuk pelet, yang kemudian digunakan sebagai target dalam pembentukan film tipis Fe-C pada substrat Si(100) menggunakan teknik *sputtering*. Selanjutnya, terhadap film tipis Fe-C dilakukan implantasi ion. Sumber ion implantasi adalah gas argon (Ar), untuk menumbuhkan *CNT* sampai dosis 5 x 10^{15} ion/cm^2. Pembentukan fasa *CNT* diidentifikasi dengan *XRD*, dan morfologi permukaannya diamati dengan *SEM*. Hasil penelitian ini, ditunjukkan bahwa komposit Fe-C hasil *milling* memiliki ukuran serbuk sampai skala nano. Hasil identifikasi dengan *XRD* menunjukkan bahwa puncak difraksi C dan Fe terbentuk. Disisi lain, pengamatan permukaan film tipis Fe-C menunjukkan telah terbentuk *CNT*.

Kata kunci : *Carbon Nanotube*, Sistem Sensor Terintegrasi, Komposit Fe-C, Implantasi Ion

INTRODUCTION

The interest in nanosized materials have spread to other disciplines of physics, chemistry and medicine due to the possible technological application associated with them apart from the fundamental aspects [1,2]. Among the various materials, carbon is an attractive candidate to explore electric and magnetic properties and their carbide, providing stability and control over the particle size distribution [3].

Carbon-iron (C:Fe) based system are growing interest due to their improved electric and magnetic properties as well as in their potential application as sensors, catalyst, and in the potential reduction of the cost required to produce bulk quantities [3-6]. Nanocomposite and nanostructure of carbon containing iron nanoparticles exhibit the properties of both constituents, i.e., electric and magnetic as well as conducting, have proved to be a useful filler material for electromagnetic shielding applications in the form of coating or film [7,8].

On the other side, there has been great interest in the electrical properties of carbon nanotubes (CNT), as CNT-based molecular electronics offers significant potential as a nanoscale alternative to silicon based devices [9-14]. CNT offers promise for future nano electronic applications, and reliably controlling CNT growth has been a big challenge. CNTs exhibit high conductivity and great stability, making them promising candidates for nano-electronics and for sensor device. As-grown devices can have a number of different nanotubes, which can be either metallic or semiconducting and also vary in diameter. These factors affect the electrical properties, which are important in particular for chemical sensing application [15]. It has been reported that CNT could be created through defect using Focused Ion Beams (FIB) that significantly affected the electrical transport and transistor-like behaviour [16]. An ability to artificially introduce or control such defect is highly desirable. The defect can be additive, by adding additional material to introduce localized strains for affecting the CNT properties, or insert catalyst particles. In this study, we tried to artificially introduced such defect by implanting Argon ion on Fe-C thin film, as a first step for the future exploration of CNT of their effect on the electrical properties of the manipulated nanotube morphologies.

EXPERIMENTAL METHOD

The raw materials used in this research are graphite powder (Carbon, C) prepared by Merck and the iron powder (Fe) from Aldrich. The purity and particle size of raw materials used in this study are presented in Table 1.

Graphite powder and iron powder were weighed 10 grams each, then the powder is inserted into a large stainless steel vial (50 mL). The milling process conducted for 50 hours at room temperature (RT) using High Energy Milling (HEM) facility. Weight ratio of balls to sample was approximately 3 : 2.

To avoid damaging the milling equipment due to high increasing motor temperature, then for each cycle of 90 minutes milling, the process was stopped about 30 minutes for the purpose of cooling the motor. In this milling process vial and balls used are made of stainless steel. Then the mixture of graphite and iron powder obtained from milling was weighed and 8 grams of it was pressed with a press machine up to pressure of 15 Tons. A press machine used is hydraulic type, brand of Daiwa Universal Testing Machine, with the following specifications: rat 100, capacity 100 tons, a power source voltage is 220 VAC, made by Daiwa Kenko, Co. Ltd. A press machine is located at the Faculty of Civil and Environmental Engineering, ITB-Bandung. When the pressure reaches 5 tons/cm^2 of pressing machine, the pressure was held for 5 minutes to complete the formation of pellets so that pellets are strong and not easily broken. A formed pellet has the dimension of 2.5 cm in diameter with a thickness of 0.5 cm.

Table 1. The raw materials used in this research.

Material	Purity (%)	Particle size (μm)
Graphite	99.5	10
Iron	99.9	10-50

Furthermore, the above formed Fe-C pellet then used as targets in the fabrication of Fe-C thin film on the substrate of Si (100) using DC-sputtering technique. The parameter of sputtering were the substrate temperature of 300 ^{o}C, deposition time of 3 hours, the current value of 0.033 A, the voltage of 600 V, the vacuum pressure of about 3.3 x 10^{-2} Torr. The equipment of DC-Magneton sputtering that we used here was the equipment located at the Faculty of Mathematics and Natural Science, ITB-Bandung.

The next stage was ion implantation of Fe-C/Si thin film using irradiation of argon ion. Parameters when conducting doping ion implantation were 70 keV of doping energy, 5 x 10^{15} ions/cm^2 of dose implantation (D), 20 mA of current (I), 10^{-5} mbar of vacuum level, 1.603 x 10^{-19} of Ar electron charge (e), and 12.566 cm^2 of the sectional area of ion beam source (L). The doping time after calculating by inserting the above parameters to the formula of

$$D = \frac{I(A) \times t(dt)}{e \times L} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

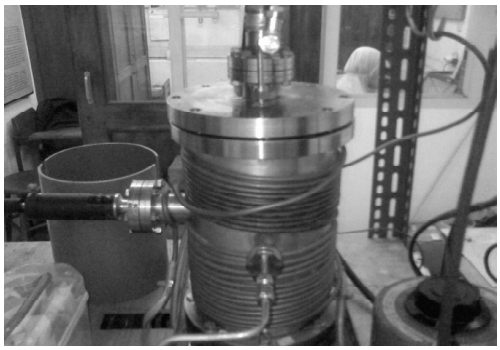
which found around 510 seconds.

The equipment of sputtering and ion implantation used in this study is showed in Figure 1. The crystallographical phases of milling powder, Fe-C thin film before and after bombarded by Ar ion implantation were determined using X-ray Diffraction (XRD) patterns taken with a Phillips APD 3520 diffractometer, using Cu radiation, which are located at Nuclear Characterization and Analysis Division (BKAN), PTBIN-BATAN. The morphology of milling powder and thin film has been observed and studied by JEOL Scanning Electron Microscope (SEM).

RESULTS AND DISCUSSION

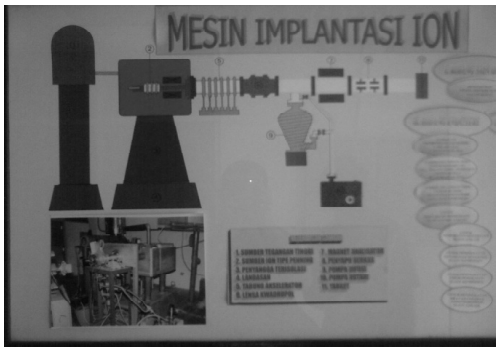
X-Ray diffraction patterns of Fe-C composites before and after the milling process is shown in Figure 2. XRD profiles showed that the mixture powder does not contain impurity and consisted only of C and Fe phases. From this pattern could be detected the diffraction peak of carbon atom C (002), C (004) and Fe (110) could be detected. Carbon peak intensity of C (002) is higher than the peak of C (004) indicates that the graphite structure is still dominant, dominated by the hexagonal phase, because other diffraction peak of C was not identified. The identified of asymmetric peak of

Volume 11. No. 1, Oktober 2010, hal : 64 - 69
ISSN : 1411-1098

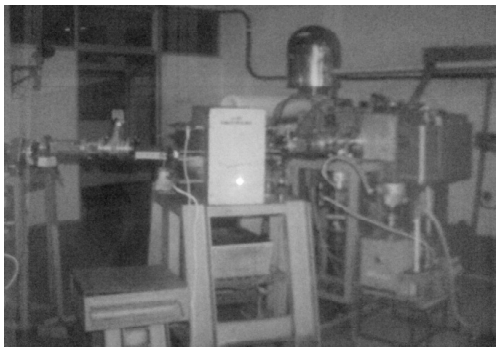


The Chamber of Sputtering Equipment

The Control Device of Sputtering Equipment



The Scheme of Ion Implantation Equipment



The Figure of Ion Implantation Equipment

Figure 1. The photograph of sputtering equipment and ion implantation equipment used in this study.

C(002), possibly due to the presence of amorphous carbon phase. Amorphous phase that was dominant, as seen in Figure 2, was also found in the sample of graphite powder without Fe that has been processed by milling over 50 hours [17].

Next is the morphology observation on the surface of Fe-C powders after milling processed by using

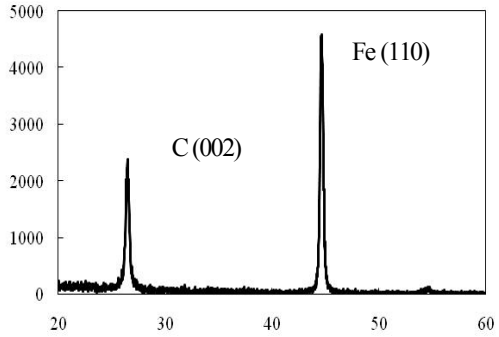


Figure 2. X-ray diffraction patterns of Fe-C powder milling results for 50 hours.

HEM technique for 50 hours, in order to determine the range of powder particle size. It is expected that after the milling process for 50 hours, the powder has a nano-sized particles, thus increasing the quality of Fe-C thin film growth when the powders of nano-sized Fe-C is used as a target of sputtering. As shown in Figure 3, it is shown that the Fe-C powders has been destructed caused by the vial ball of HEM, long flat and some powder into a clot (*upper photograph*). When viewed at a magnification of 10.000 times of SEM results (*bottom photograph*), it is shown that the average size range of powder is 100-200 nm. Powder tends to coalesce and form a phase with a small powder size, where there are already fining into fragments, and some fragments fused with other fragments in the opposite direction.

The theory of this milling process (mechanical alloy) is that the used vial balls collide with each other

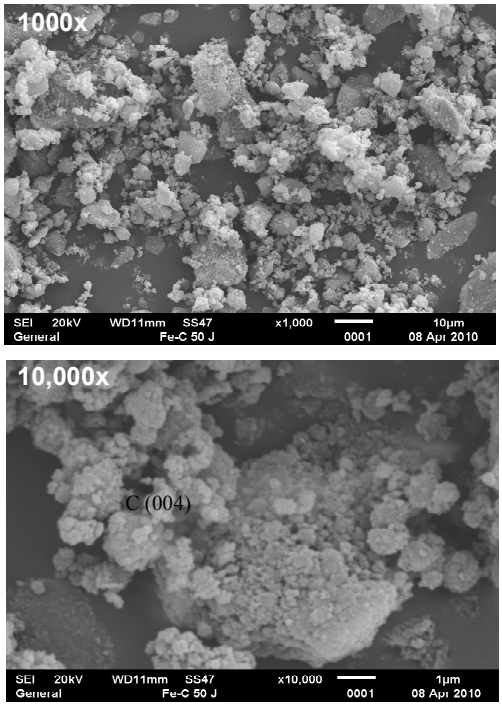


Figure 3. The SEM observation of surface morphology of Fe-C powder after milling processed using the technique of HEM for 50 hours (upper is 1000x magnification, bottom is 10,000x magnifications).

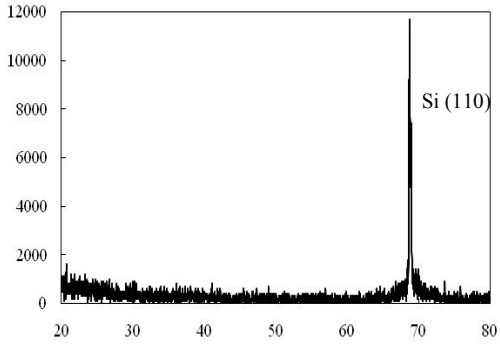


Figure 4. X-ray diffraction patterns of Fe-C thin film fabricated by DC-Sputtering.

cause fracture, then step of cold welding (cold pooling) is happened. The step through this mechanical alloy is four steps. First is flattening process from round to flat and then followed by welding predominance, second is formation of powder in the same direction, third is random orientation unification, and the last step number fourth is the steady state [18]. Figure 3 shows some of fragments together in the opposite direction with the powder has a fine size and small enough, so that the estimated results of powder milling process using HEM technique for 50 hours had passed until the 4th step above.

Next, the Fe-C powder as a results of milling process by HEM technique for 50 hours, which has nano-sized structure (from the result of SEM) and contain no impurity (from the result of XRD), was pressed in order to be used as a target in the fabrication of Fe-C thin film using sputtering (see Figure 1 for experimental equipment).

The XRD pattern of the thin film was presented in Figure 4. The peak of XRD pattern appears at the angles of 68.74^{o}, is the one peak of Si(100) substrate used in the fabrication of thin film. Unfortunately, from the results of XRD, the peak of Fe and C phase still could not be detected, as it has been shown in the XRD results of Fe-C powder, which is the compiler of the target material sputtering. Possibility the crystallization of Fe and C elements is still not happened, so that tends to thin film is still in the phase of amorphous. In the fabrication of Fe-C thin film this time, sputtering temperature was set to 300 ^{o}C, therefore it is estimated that the crystallization of Fe-C still has not happened at this temperature, and as an improvement in the future need to raise the temperature sputtering.

Furthermore, to determine the level of homogeneity of the thin film, the observations were carried out using SEM. The homogeneity level of the thin film plays a very crucial role, especially to find out the possibility of the formation of CNTs on the surface of thin film, and to generate the magnetic and electrical characteristics of the film. From Figure 45 (*left*) that shows the surface morphology of Fe-C thin film, it is shown that the film has a smooth condition, and also appears evident that the Fe-C particles have been deposited on the surface of the Si(100) substrate, which is marked by

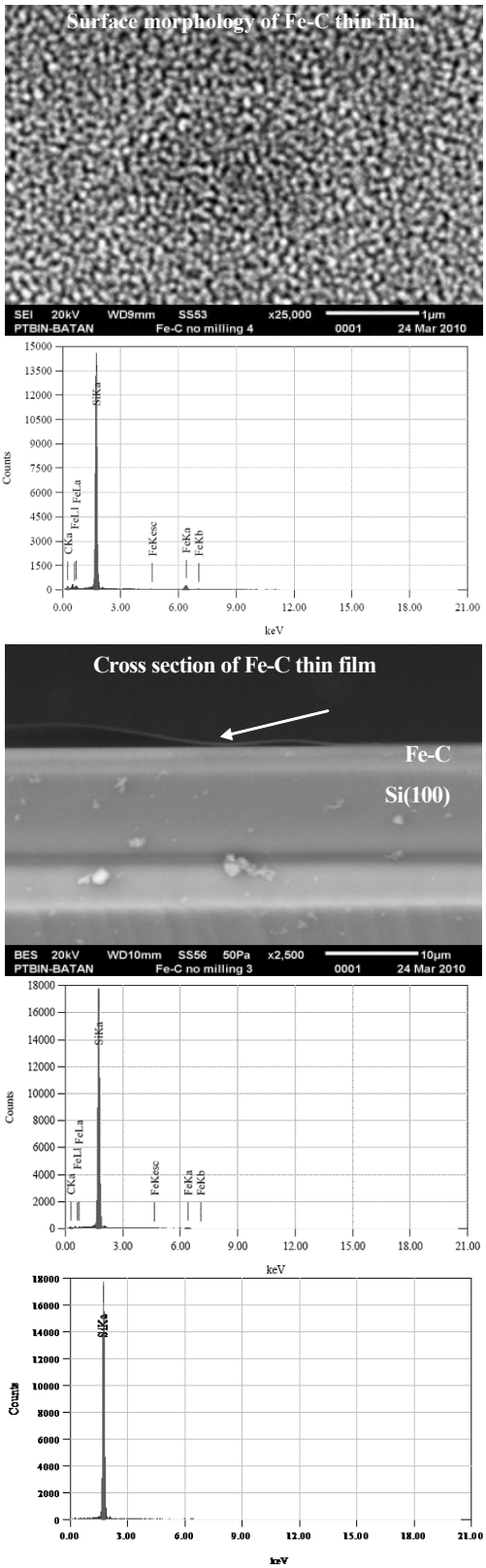


Figure 5. SEM photograph of the Fe-C thin film on Si(100) at the sputtering temperature of 300 ^{o}C, deposition time of 180 minutes and vacuum chamber of 3.3 x 10^{-2} Torr. Upper photograph present the microstructure of surface morphology of Fe-C thin film and the result of EDX at the surface. Bottom photograph present the cross section of Fe-C thin film after Ar^{+} ion implantation and the result of EDX at the cross section.

Volume 11. No. 1, Oktober 2010, hal : 64 - 69
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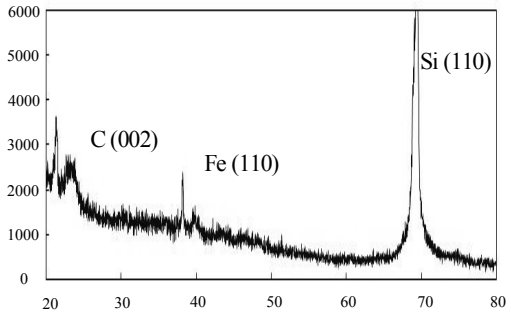

Figure 6. X-ray diffraction patterns of Fe-C thin film after doped by Ar^+ ion implantation.

a round white object evenly dispersed on the surface of the Si(100) substrate. To measure the thin film thickness is also used SEM by shooting a sample from cross direction. The Fe-C thin film deposited above the Si(100) substrate can be shown in Figure 5 (*right*), where the thin film thickness is around 1 μm.

Furthermore, the Ar+ ion implantation process was carried out to the Fe-C thin film fabricated by DC-Sputtering, with a dose of $1x10^{17}$ for 8 minutes, as a technique to make Fe from Fe-C as a catalyst nanoparticle for growth of carbon nanotubes (CNTs). From Figure 5, on the top surface of the film, looks a piece of fiber, which is estimated to the embryo of CNT formation, but need to clarify using TEM observation. On this paper, unfortunately not yet to explain the observation using TEM, and this will be the subject of research in the future search.

Firstly, the clarification of phase on Fe-C thin films was carried out using XRD. In contrast to the phase which was detected in Fe-C thin film before ion implantation, beside a very dominant Si(100) peak, a peak of Fe(110) and C(002) were also found although with a weak peak (see Figure 6). The XRD of thin film after ion implantation is rather similar to the results of XRD powder after processed milling. When compared with the results of XRD of Fe-C mixing powder after processed by milling technique, the angle of Fe and C peak shift 4 degrees to the left. Angle peak of Fe(110) shift from 44.77 to 40.32, and the angle peak of C(002) shift from 26.73 to 22.02. The peak intensity of Fe was also decreased very sharply.

This fact is an evidence of the occurrence the formation of Fe catalytic nanoparticles from Ar^+ ion implantation. These catalytic nanoparticles will be used as an initial of growing CNT. Details discussion of the mathematical calculation related to the shift angle and its support from data analysis of TEM will be given in a separate papers, because at the time of completeing this paper, the TEM analysis has not been carried out.

From observed and described above, the following is predicted happened in the growing of carbon nanotubes by applying the bombardment of Ar^+ ion. First, in the surface of Fe-C thin film, after implanted by Ar^+ ion, the Fe atom from Fe-C thin film aggregated to form Fe-cluster which acts as a precursor for the formation of Fe catalytic nanoparticles. Consequently, at the same time, in the initial stage of Ar^+ ion implantation, upon further aggregation, the catalytic Fe-particle would emerge, and with the continual supply of ion-induced carbon source, various carbon nanotubes would form.

CONCLUSIONS

From the result of this experiment can be concluded as follows:

1. Fe-C mixing powder does not contain impurity and consisted only of phase C and Fe, which the peak detected are peak of carbon atom C (002), C (004) and Fe (110).
2. After milling process for 50 hours, the powder has a nano-sized particles, with the average size range of powder is around 100-200 nm.
3. The phase peak of Fe and C still could not be detected from the Fe-C thin film fabricated by DC-Sputtering technique before doping ion implantation. Possibility the crystallization of Fe and C elements is still not happened, so that needs an improvement in the future to raise the temperature sputtering.
4. The Fe-C thin film deposited above the Si(100) substrate has a thickness of around 1 μm, smooth and flat morphology. On the top surface of the film, looks a piece of fiber, which is estimated to the embryo of CNT formation, but need to clarify using TEM observation.
5. The phase of Fe-C thin film after ion implantation has a very dominant Si(100) peak, a peak of Fe(110) and C(002). The angle of Fe and C peak shift 4 degrees to the left. Angle peak of Fe(110) shift from 44.77 to 40.32, and the angle peak of C(002) shift from 26.73 to 22.02.

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