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SYNTHESIS AND CHARACTERIZATION OF GRAPHITE NANOSTRUCTURE THIN FILM WITH SPUTTERING TECHNIQUE

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF GRAPHITE NANOSTRUCTURE THIN FILM WITH SPUTTERING TECHNIQUE. Synthesis and characterization of graphite nanostructure thin film using the DC-sputtering technique has been carried out. Nanostructured graphite for target of deposition using DC-Sputtering technique has been prepared by milling technique using High Energy Milling (HEM) with the variation of milling time between 50 hours until 100 hours. First, the graphite target was prepared by doing a compaction using press machine to the nanostructured graphite powder got from milling process. Secondly, a thin film of graphite was fabricated using DC-Sputtering technique. The phase identification of nanostructured graphite thin film were carried out using X-Ray Diffraction (XRD), and the surface and cross section morphology of thin film were observed using Scanning Electron Microscopy (SEM). XRD identification shows the presence of peaks of Si(100) and C(002) in all conditions of preparing powder using for target, but a shift of the angel's peak to the left and the decreasing of peak intensity were found. While the observation using SEM to surface morphology of thin film shows that the form of thin films are mostly homogeneous, smooth and flat at the milling time of 50-75 hours. From the SEM photograph of cross section, it is shown that there is a tendency of the more commonly found particles of droplets on the surface of thin film with the increasing of milling process against the carbon powder as a constituent of pellets for the DC-Sputtering targets, especially in the case of C/Si thin film fabricated using target prepared by milling for 100 hours, the morphology of surface was worst.

Key words : Graphite Thin Film, Nanostructure, DC-Sputtering Technique, HEM, Carbon Target

ABSTRAK

SINTESIS DAN KARAKTERISASI FILM TIPIS GRAFIT BERSTRUKTUR NANO DENGAN TEKNIK *SPUTTERING*. Telah dilakukan sintesis dan karakterisasi film tipis grafit berstruktur nano menggunakan teknik *DC-sputtering*. Grafit berstruktur nano dibuat melalui proses milling dengan teknik *High Energy Milling* (*HEM*) dengan variasi waktu milling antara 50 jam sampai 100 jam, yang selanjutnya digunakan sebagai target pada teknik *DC-Sputtering*. Pertama, target grafit dibuat dari serbuk grafit berstruktur nano hasil proses milling yang dikompaksi dalam bentuk pelet dengan menggunakan mesin pres. Kedua, film tipis grafit dibuat dengan menggunakan teknik *DC-Sputtering*. Identifikasi fasa film tipis grafit berstruktur nano dilakukan menggunakan *X-Ray Difraksi* (XRD), dan pengamatan morfologi permukaan dan penampang lintang film tipis diamati dengan menggunakan *Scanning Electron Microscope* (*SEM*). Identifikasi *XRD* menunjukkan adanya puncak dari Si (100) dan C (002) untuk semua kondisi pemrosesan serbuk untuk target, namun ditemukan pergeseran sudut difraksi ke kiri dan puncak intensitas difraksi menurunan. Sedangkan observasi dengan menggunakan *SEM* untuk morfologi permukaan film tipis menunjukkan bahwa bentuk film tipis sebagian besar homogen, halus dan rata untuk proses *milling* selama 50 jam hingga 75 jam. Dari foto *SEM* untuk penampang lintang, terlihat bahwa ada kecenderungan partikel dalam bentuk droplet pada permukaan film tipis seiring dengan meningkatnya waktu *milling* terhadap serbuk karbon sebagai konstituen dari pelet sebagai target pada teknik *DC-Sputtering*, terutama dalam hal film tipis C/Si yang dibuat menggunakan target yang disiapkan melalui proses *milling* selama 100 jam, menunjukkan morfologi permukaannya kurang bagus.

Kata kunci : Film tipis grafit, Nanostruktur, Teknik *DC-Sputtering*, *HEM*, Target karbon

Vol. 14, No. 1, Oktober 2011, hal : 59 - 64
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INTRODUCTION

In the last few years, studies on amorphous carbon (a-C) and carbon based thin films have been extensively reported. These films find wide applications in micro electronic devices, due to their important electrical and mechanical properties. Amorphous carbon films show a wide energy band gap, and have been used as window layer in hydrogenated amorphous silicon based solar cells, for the enhancement of open circuit voltage and for improving the short wavelength response. Thin films of a-C are ideal protective coating for magnetic and optical disks [1-5].

Unprecedented worldwide activity in the investigation of elemental carbon was initiated by the discovery of the C-60 molecule [6] and the development of the arc discharge technique [7] to produce new carbon allotropes in macroscopic quantities. This field is still growing rapidly, and the interest seems to shift gradually from the basic fullerene molecules actually [8]. Discovered the carbon nanotubes which are, from a technological point of view, considered to be the most promising members of the family of carbon nanoparticles [9,10].

Several synthesis techniques have been known to synthesis carbon nanostructure thin films, such us chemical vapor deposition (CVD), system evaporation and sputtering systems [11-15]. In this research, first a High Energy Milling (HEM) technique will be used to grow the carbon nanostructure, and second then the prepared carbon nanostructure is used as a pellet target for deposition process using DC-sputtering technique. In current research of nanomaterials using thin film synthesis method, the surface morphology of thin film become critical point, which the structure of target take an important role in preparing of good and smooth thin film. Therefore, we are trying to fabricate a nanostructure target in advance, in order to produce good and smooth graphite thin film that also has a nanostructure, so that in future we can improve the feature and properties of the produced thin film.

EXPERIMENTAL METHOD

Materials

The raw materials used in this research are graphite powder (Carbon, C) produced by Merck, that has a high purity level of 99.5%, with the powder particle size of 10 μm.

Equipments

The equipment used in this research are analytical scales, High Energy Milling (HEM) equipment brand CertiPrep Spex 8000M Mixer/Mill and the X-ray diffractometer (XRD) equipment brand Philips APD 3520, which are located at the Division of Nuclear Characterization and Analysis (BKAN), PTBIN-BATAN. The hydraulic pressing machine Testing Machine Universal Daiwa brand manufatured by Daiwa Kenko, Co. Ltd., which is located at the Faculty of Civil and Environmental Engineering, ITB - Bandung. DC-Magneton sputtering equipment used here is located at the Faculty of Mathematics and Physics Department, ITB - Bandung. The JEOL-High Resolution Scanning Electron Microscopy (HRSEM) equipment is located at the Division of Nuclear Industry Materials (BBIN), PTBIN-BATAN.

Procedure

Graphite powder material was prepared for 20 grams, and then the powder is inserted into a large vial container (50 cc) made of stainless steel. After that, the powder mixture is processed by milling techniques for 50 hours, 75 hours and 100 hours for each. Weight ratio of ball : sample weight was approximately 3 : 2 in a large vial at room temperature (R.T). To avoid damaging

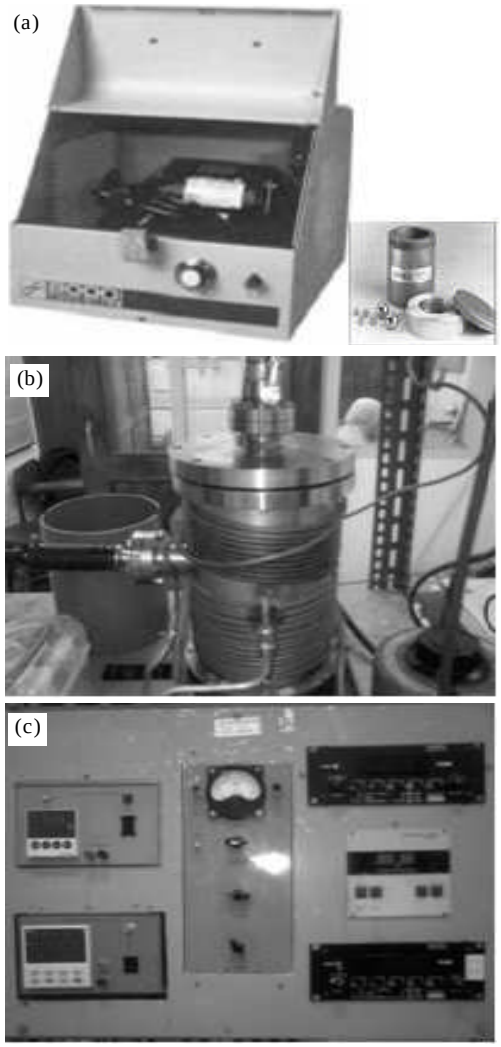


Figure 1. (a). The photograph of HEM equipment and (b). Chamber of DC Sputtering Equipment and (c). Control device of DC sputtering Equipment

the milling equipment due to increased motor temperature is too high, then for each cycle during the 90 minutes of milling, the process was stopped about 0.5 hours for the purpose of cooling the motor. In this milling process vial and balls used are made of stainless steel.

The surface morphology of the milled graphite powder were observed by SEM in order to determine the particle size of graphite. Then 3 grams of powder was pressed with a press machine up to power press of 40 Tons. A formed pellet has a dimension of 25 mm in diameter with a thickness of 5 mm.

Furthermore, formed pellet then used as target of deposition in the fabrication of graphite thin film using DC-sputtering technique. The parameter of sputtering were the substrate temperature of 573 K, deposition time of 1.08×10^4 seconds, the current value of 0.033 A, the voltage of 600 V, the vacuum pressure of about 3.3×10^{-2} Torr. Substrate used in this experiment is Si (100).

Carbon nanostructure thin film is formed and then characterized by XRD, and HRSEM methods. HEM equipment and DC-Magneton Sputtering equipment is shown in Figure 1.

RESULTS AND DISCUSSION

The 20 grams of graphite powder was processed using HEM technique for 50 hours, 75 hours and 100 hours at room temperature. After milling process, observation on the surface morphology of graphite powders by SEM were carried out, in order to determine the range of powder particle size. It is expected that after milling process, the graphite powder has a small-sized particles, and the size of particle decreases with the increasing of milling time. Figure 2 shows the surface morphology of graphite powder observed by SEM. It is shown that the particle size of graphite has been decreased until the size of nano order. At the magnification of 3500 times of SEM, it is shown that the average size of particle powder is aorund 70-250 nm [16]. The particle size of graphite powder after milling process for 50 hours is about 250 nm, for 75 hours is about 150 nm and for 100 hours is about 70 nm, respectively. It is shown that the graphite powder has been destructed caused by the vial ball of HEM, and generated a particle with the form of long flat and some powder changes its form became a clot. 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. Finally as a conclusion, the HEM technique can be used as a technique for fabricating graphite powder with nanometer size.

Theoretically, at milling process (or called as mechanical alloy) that is used vial balls, the collide between particle powder will cause fracture, then the

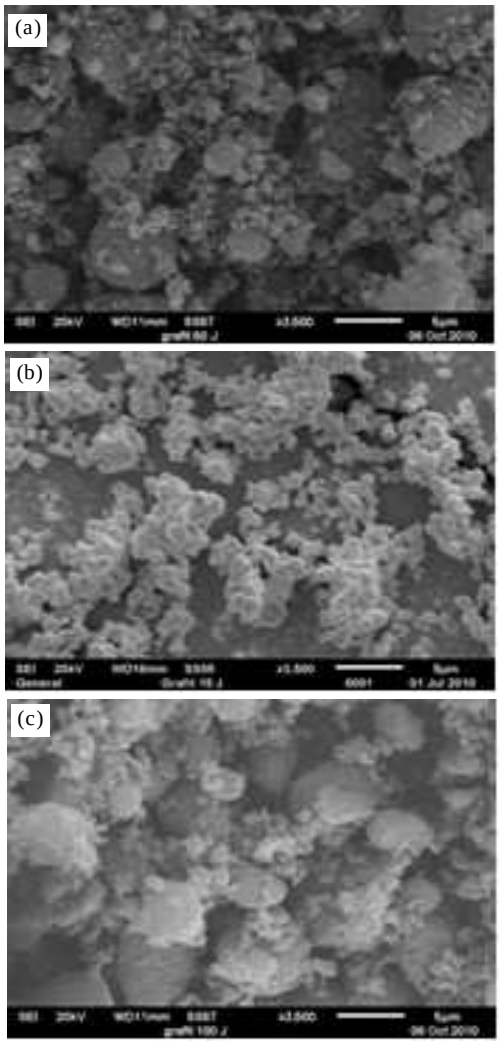


Figure 2. The SEM observation of surface morphology of graphite powder after milled using the technique of HEM for (a). 50 hours, (b). 75 hours and (c) 100 hours.

step of cold welding (or called as 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 [17]. Figure 2 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 up to 100 hours had passed until the 4th step above.

To observe the crystal structure of thin film fabricated by DC-Sputtering technique, XRD methods was used. In this experiment, a nanostructure thin film of graphite was fabricated by DC-Sputtering technique on Si (100) substrate, and graphite pellet created from milled powder with variation of milling time from 50 hours up to 100 hours was used as a target. In the fabrication of graphite thin film, the deposition temperature was 300°C, deposition time was 3 hours, the current value was 0.033 A, the voltage was 600 V, and the vacuum

Vol. 14, No. 1, Oktober 2011, hal : 59 - 64
ISSN : 1411-1098

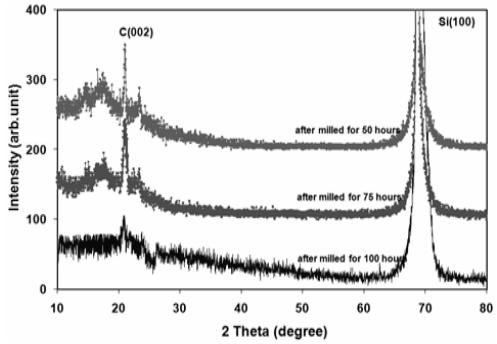
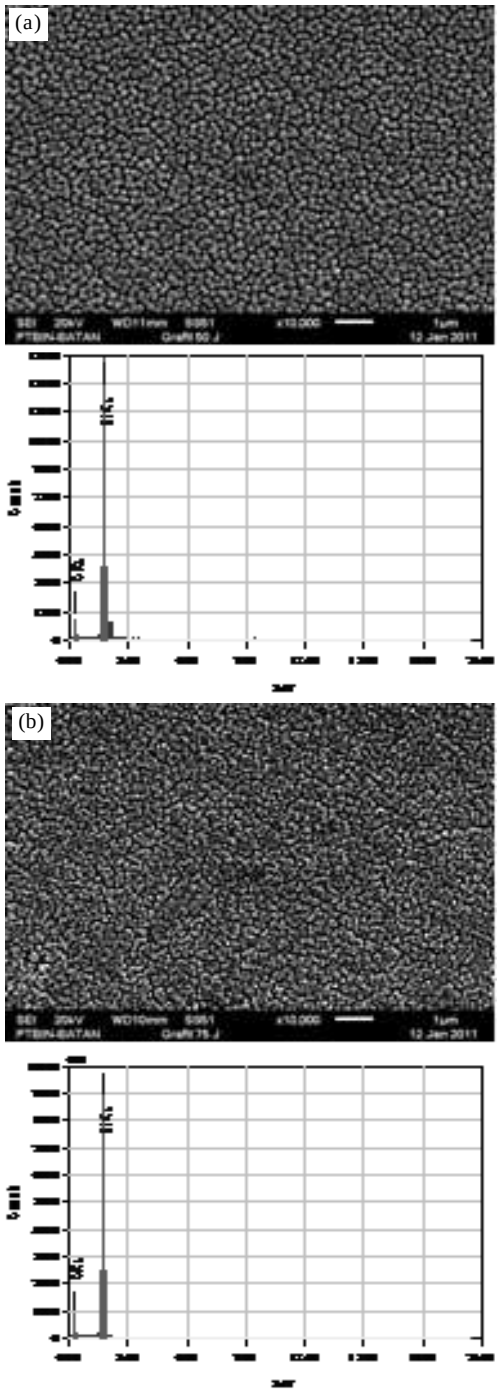


Figure 3. XRD pattern of graphite thin film using graphite target prepared from powder that was prepared by milling for 50-100 hours.



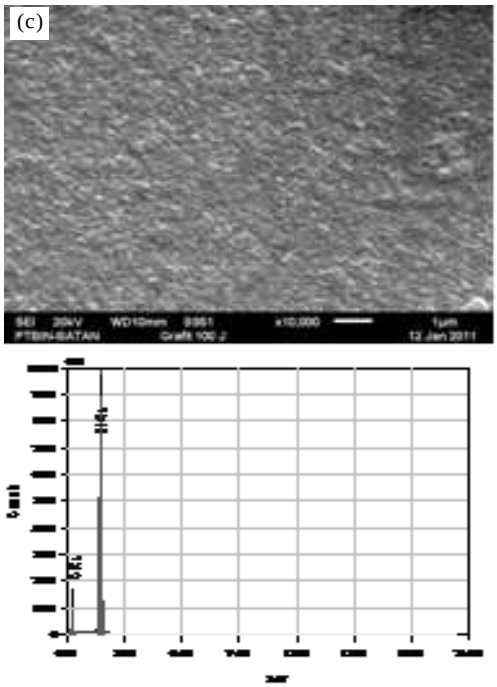


Figure 4. SEM image of surface morphology and EDS data of graphite thin film using graphite target created from powder that was prepared by milling for (a). 50 hours, (b). 75 hours and (c). 100 hours

pressure was about 3.3 x 10^{-2} Torr. The observation of a spectrum from XRD pattern was obtained and presented in Figure 3. The peak of C(002) was detected at the angles of 23.94^{o} (after milled for 50 hours), the peak of Si(100) was detected at the angles of 68.74^{o}, which is assumed as a peak of Si(100) substrate used in the fabrication of thin film. The intensity of C(002) peak was decreased drastically as long as the increasing of milling time process.

Furthermore, to determine the level of homogenity of the thin film, the observations were carried out using HRSEM, as shown in Figure 4 that shows the surface morphology of graphite thin film. It is shown that the film has a smooth condition, and also appears evident that the graphite particles have been deposited on Si(100) substrate, which is marked by a round white object evenly dispersed on the surface of Si(100) substrate.The result of observations show that those thin film has a homogeneous morphology, with a high population density, and not much of droplet particles that is one of the problems of sputtering technique was found. At a magnification of 10.000 times of SEM shows that the particle size of graphite became smaller and smaller with the increasing of milling time, and the average size of particle powder is around 50-150 nm. In accordance with the particle size of graphite powder used as a target, the smaller the particle size of graphite as target then formed on the thin film is also getting small. Figure 4(a) seems that milling time of 50 hours , Figure 4(b) seems that milling time of 75 hours and

the graphite particles seen clearly, while milling time of 100 hours appears to form agglomeration (Figure 4(c)). For comparison, below is shown a photograph of the surface morphology of graphite thin film, produced using the same DC-Sputtering. However, the target used is composed of graphite powder standard, which was not done a process of milling. From the photograph, it looks that graphite thin film has an uneven surface morphology and a little rough. On the surface of the graphite thin film is also found several small holes and the large particles of droplets that may disrupt or reduce the properties of the graphite thin film. This can happen because the constituent powder of pellet target has a particle size of several microns (μm), so that at the time of the deposition to the surface of Si(100) substrate, it is predicted the graphite particles already deposited was thrown out by the new entry of grahite particle that has a size of several micron. The surface morphology of this graphite thin film is much worse than the surface morphology of graphite thin film prepared by using a target composed of the milled powder (this milled powder has nano size particle). It has also become evident that through the use of target that is composed of nano-sized powder, it will be able to produce thin films having better morphology, smooth and homogeneous.

The observations result of cross section of graphite nanostructure thin film with HRSEM is shown in Figure 5. The result of observations show that the thin film has a thickness of around 25 to 50 nm, and from the result of EDS characterization, it is clearly shown that the graphite thin film has been performed on surface of Si(100) substrate.

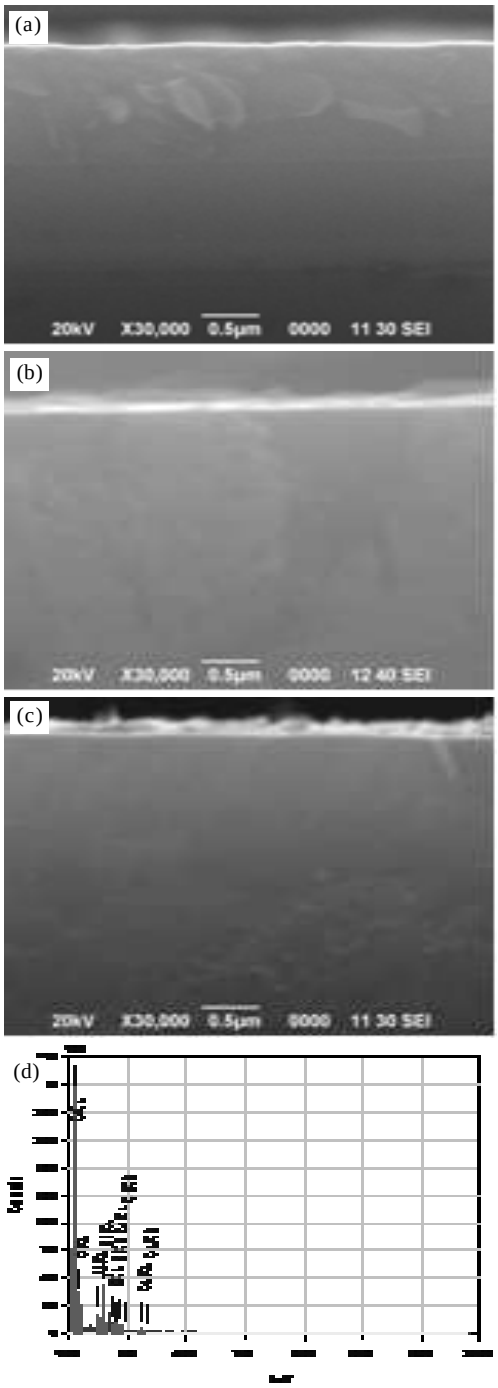


Figure 5. SEM image for cross section of graphite thin film using graphite target created from powder that was prepared by milling for (a). 50 hours, (b). 75 hours, (c). 100 hours and (d). EDS data

CONCLUTION

From this research we can conclude that the HEM technique can produce nano-sized graphite powder and the longer the milling process with the HEM technique graphite, the smaller graphite powder size was obtained. By using DC-magneton sputtering equipment, it was successfully created nanostructure thin film of graphite on the surface of Si (100) and pellets nanostructure graphite as target. The nanostructure of graphite thin layer has thickness of 25 to 50 nm.

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Vol. 14, No. 1, Oktober 2011, hal : 59 - 64
ISSN : 1411-1098

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