Woodceramics, a substance based on woody materials carbonized at elevated temperatures after impregnating with phenolic resin, have been developed as a new kind of porous carbonaceous material. To expand the industrial application, we attempted to produce amorphous carbon films were RF magnetron sputtering using woodceramics as its target. As a result, typical amorphous carbon films were successfully produced using woodceramics, and the films were characterized by X-ray diffractometry, Raman spectroscopy and X-ray photoelectron spectroscopy. The films produced were composed of carbon turbostratic structure or amorphous whose electron configurations consisted of sp\(^2\) and sp\(^3\). The ratio of sp\(^3\) bonding in the films were about 53% just after the sputtering, but the number increased to about 82% after etching the material using argon ions. Fundamental mechanical properties such as hardness and friction coefficient were also measured and taken into account.

Key words: woodceramics, amorphous carbon film, magnetron sputtering, X-ray photoelectron spectroscopy, Raman spectroscopy

1. INTRODUCTION

Due to the fact that industrial waste pollution coupled with carbon dioxide emission has been a serious global concern for environmentalists, recycling and reusing have become a social norm. Woodceramics (WCMs) has been receiving attention as new environment friendly material (eco-materials) produced by carbonizing compressed mixtures of charcoal originating from waste woody chips and phenolic resin in a vacuum [1], have been recently developed. After being carbonized by heating the waste in an inert atmosphere, the phenolic resin transforms into a hard glass-like carbon and the woody materials changed into soft amorphous carbon [2]. They have a high percentage of carbon elements, quite good properties for electrical resistance, electromagnetic shielding and infrared radiation shielding are being expected to be used in a wide variety of industrial fields, such as wear-resistant materials, heat insulator, infrared radiators and etc [3-4].

On the other hand, carbon forms a great variety of crystalline and disordered structures. Amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H) both form of amorphous carbon containing sp\(^3\) bonding and tetrahedral amorphous carbon (ta-C) contains sp\(^3\) bonding [5]. It exhibits high mechanical hardness, chemical inertness, corrosion resistance and good tribological properties. Amorphous carbon films have widespread applications as protective coating for some products such as magnetic storage disks, cutting tools, automobile, biomedical and micro-electromechanical (MEMs) parts. The amorphous carbon films have been coated by various chemical vapor deposition (CVD) and physical vapor deposition (PVD) techniques. The conventional RF magnetron sputtering is one technique for production amorphous carbon films with high deposition rates, low deposition temperature, high forming quality. [6-8].

In this study, we attempted to low costly deposit amorphous carbon films through a RF magnetron sputtering technique replace high purity graphite with using woodceramics as a target to explore a further area of application for woodceramics. The aim of this study is to investigate the microstructures and the characters of produced films by the analysis of X-ray diffractometry, ratio of sp\(^3\)/sp\(^2\) by Raman spectroscopy and X-ray photoelectron spectroscopy [9]. Some fundamental mechanical properties such as hardness and friction coefficient were also reported in the observation.

2. EXPERIMENTAL PROCEDURE

2.1 Fabrication of WCMs (target material)

Some pieces of medium-density radiated pinewood was firstly carbonized into charcoal, crushed and milled into a powder. The powder was mixed with phenolic resin and the mixtures were poured into a graphite mold to produce woodceramics plates whose sizes were 30 mm in diameter. The forming process start from heated mold to 773 K under compress force 10 MPa hold for 10 minutes, specimen will form to 5 mm in thickness. The temperature of a furnace was raised at a slow heating rate of \(<275 K/min\) to final carbonized temperature at 1473 K. [10]. The final products (disk plates) are porous carbonaceous materials called “woodceramics”, which were used as the target in this study.
2.2 Fabrication of amorphous carbon Films

The amorphous carbon films were deposited by a RF magnetron sputtering (PLASMAN Model CSP-III-SPT-S2, SS Alloys Co. Ltd.) with a RF power of 100 W and frequency of 13.56 MHZ.

The substrates were silicon wafers, which were cleaned by ultrasonic 15 minutes before deposition. The schematic of sputtering was shown in Fig.1. The distance between the target and substrate setting was 32 mm. After the deposition chamber was evacuated to 4.5×10⁻⁷ Pa, feed argon gas with flow rate 20 mL/min into chamber. The films were deposited at room temperature by slowly increasing RF power to 70 W, the surfaces were pre-sputtered for 5 minutes before the actual coating [11]. After slowly raising the RF power, the temperature held constant hold coating for 30 minutes.

2.3 Analyses

X-ray diffraction (XRD) measurements were made for the substrate after deposition using a Rigaku Ultima IV to determined crystal structures of the samples using Cu-Kα radiation at 40 kV and 45 mA at room temperature(wave length of 1.541 Å). The Raman spectra were obtained using a JASCO NRS-2100 laser Raman spectrophotometer, which was operated at a laser wavelength of 488 nm. The laser power was 30 mW and the spot size was 2 mm. The spectra were taken from 1100 to 2000 cm⁻¹ with a resolution of 2 cm⁻¹. X-ray photoelectron spectroscopy (XPS) studies were also carried out using a Shimadzu Kratos Axis-Ultra DLD. The XPS peak positions that reflect the electron binding energies for specific atomic levels can be used to identify the chemical states of the structure.

2.4 Mechanical tests

The fundamental mechanical properties of the films were measured using a ball-on-disk friction tester (CSEM; Tribotester). In the friction test, a dry sliding test was carried out using a ball indenter, made of type 440C stainless steel (diameter of 6.0 mm) under a normal applied load of 3 N, and the disk rotation of 6000 rpm. The tests were performed under ambient air at room temperature with 30–45% humidity [12]. The hardness of the amorphous carbon films was measured by a Vickers’s microhardness tester [13].

Fig. 1 Schematic RF magnetron sputtering.

The scanning electron micrographs of (a) charcoal of radiated pinewood and (b) Woodceramics.

3. RESULT AND DISCUSSION

The scanning electron micrographs for charcoal obtained from radiated pinewood was shown in Fig.2 (a) and the WCMs cross-section surface obtained porosity inside was shown in Fig.2 (b).

The results of XRD pattern investigations of the deposited films before and after etching were shown in Fig. 3. The pattern of graphite powder was included in this figure for a comparison to show that there was one strong peak at 26.38° and two weak peaks at 42.30° and 44.31°, which correspond to diffractions from (002), (100) and (101) crystal plane of the graphite.

Fig. 2 Scanning electron micrographs of (a) charcoal of radiated pinewood and (b) Woodceramics.

Fig. 3 X-ray diffraction patterns for the amorphous carbon films before and after etching.

On the other hand, for the deposited substrates, a broad peak is observed at 25.36°–26.05°. These observations correspond to the (002) crystal plane of the graphite [14], the only plane detected through this observation. Furthermore, any other diffraction peaks generally observed for the typical graphite crystal possessing a high crystallinity cannot be detected, indicating that the local structure of the deposited films were turbostratic structures or amorphous.
Raman spectroscopy offers valuable information about the atomic bonds and level structure of the molecule[15]. Especially in the nanostructured carbon thin films, it has a great importance to define the structure of carbon films, which is highly sensitive to changes in the bonding configuration of carbon atom in structure [16-17]. The Raman spectroscopy for amorphous carbon films reported previously generally consisted of two peaks around 1345-1355 cm$^{-1}$ and 1570-1590 cm$^{-1}$, which correspond to D peak and G peak respectively. The result of Raman spectroscopy for a deposited film was shown in Fig.4, there were two peaks centered at 1379 cm$^{-1}$ and 1575 cm$^{-1}$. The G band is ascribed to graphite like layers of sp$^2$ micro domains (bond stretching of all pairs sp$^2$ atoms in both rings and chains), while the D band is ascribed to the bond angle disorder in the sp$^2$ graphite like micro domains induced by the linking with sp$^3$ carbon atom (breathing modes of sp$^3$ atoms in rings). The intensity ratio of D and G peaks, $I_D/I_G$, the full width half maximum (FWHM) are sometimes used to make out the structure of the different carbon base materials, however it is difficult to analyze present data because of overlapping of broad D and G peaks [18-19].

X-ray photoelectron spectroscopy (XPS), which is more commonly known as electron spectroscopy for chemical analysis (ESCA), is the most powerful and reliable tool used for analyzing the composition of amorphous carbon thin film. XPS survey spectra for the film before and after etching are shown in Fig. 5. The etching was performed to remove a contaminated surface layer. It was found that the film at the utmost surface contained much more oxygen than that at the inner region from the surface. TheCls spectra of the deposited films before and after etching by argon ions are shown in Fig. 6 (a) and (b) respectively. Recently, some groups have proposed the decomposition of the Cls peak into one sp$^3$ bonding corresponding to graphite in amorphous or hydrogenated amorphous carbon and sp$^3$ bonding corresponding to tetrahedral amorphous carbon. The sp$^3$ bonding can be determined from the ratio of sp$^3$ peak area over the total Cls peak area. We deconvoluted the broad Cls spectra into three kinds of curves, which correspond to binding energies for sp$^3$, sp$^2$ and C-O bonding using a Gaussian and a Lorentzian method. These three curves as well as final fitted one are also included in Fig. 6.

The result in Table I summarizes peak position and spectrum area for each peak contains amorphous carbon (a-C) and tetrahedral amorphous carbon (ta-C) respect to ratio of sp$^3$ before and after etching. Before etching, ratios of sp$^3$, sp$^2$ and CO bonding were about 31 %, 27 % and 27 % respectively, while those after etching were 56 %, 12 % and 17 % respectively. There seems to be much CO contaminated phase in the present films. The ratio of sp$^3$ was about 53 % before etching by argon ions, but it increased to 82 % after etching, probably because of decrease in surface contamination and/or an oxygen-rich film. It has been reported that films surface layer are often slightly richer in sp$^2$ bonding than in the bulk [20-23], which agrees well with present results.