Influence of Different Thicknesses on Mechanical and Corrosion Properties of a-C:H Films


Abstract—The hydrogenated amorphous carbon films (a-C:H) were deposited on p-type Si (100) substrates at different thicknesses by radio frequency plasma enhanced chemical vapor deposition technique (rf-PECVD). Raman spectra display asymmetric diamond-like carbon (DLC) peaks, representative of the a-C:H films. The decrease of intensity I_D/I_G ratios revealed the sp^3 content at different thicknesses of the a-C:H films. In terms of mechanical properties, the high hardness and elastic modulus values showed the significant influence on the mechanical properties, tribology and cutting tools [1-3]. For mechanical properties, the pico-indentation hardness properties in addition, the many defects (pinholes, cracks, and scratches) on the surface as initiating point induced to redox reaction that accelerates corrosion. The corrosion severity normally depends on an aqueous solution containing types of aggressive ions, i.e., chloride ion (Cl^-), hydrogen ion (H^+), and hydroxide ion (OH^-). Those ions are absorbed at the surface of the a-C:H film, then penetrate and attack the thin films resulting in corrosion at surface [8]. More researches [8], [9] clarify that the a-C:H films provide good corrosion resistance for engineering parts. However, a part of engineering is still focused on the thickness of coating to protect the surface of substrate, which considered both the mechanical and corrosion properties.

Therefore, the aim of this study is to evaluate the thickness effect on the mechanical and corrosion properties of a-C:H films deposited on the p-type Si (100) substrate. Physical properties of a-C:H films were characterized by X-ray reflectivity (XRR) which is a non-destructive method for the determination of thin film parameters i.e., thickness, true density, and surface roughness. On the other hand, the intensity I_D/I_G ratio is characterized using a Raman spectrometer, is related to sp^3/sp^2 content ratio and H content in the a-C:H films [10]. For mechanical properties, the pico-indentation hardness test is selected in this study. There was also an enhancement detected in the pico-scale for hardness measurement of thin film. The electrochemical technique was used to analyze the results of corrosion resistance which is the potentialdynamic polarization. It is an excellent tool for indicating in terms of corrosion potential (E_{corr}), corrosion current density (I_{corr}), corrosion rate, protective efficiency and type of corrosion.

I. INTRODUCTION

HYDROGENATED amorphous carbon (a-C:H) films are extensively used in many applications such as optical devices, magnetic storage disks, biomedical parts, sliding parts and cutting tools [1]-[3]. The properties in terms of hardenability, chemical inertness and tribology are suitable for such application [4] as the results of thickness, density, mechanical and corrosion properties of films depend on each deposition technique. One of the most widely used techniques for deposition is radio frequency plasma enhanced chemical vapor deposition (rf-PECVD), where the high plasma density and the ion energy can be controlled through rf power and direct current negative bias which produces the a-C:H films [5], [6]. Although in the literature there are many reports on the improvements upon the application of a-C:H films, there are only a few studies of the effect of thickness on the mechanical properties that give formation to the elastic and plastic properties of film related to I_D/I_G ratio, G-band position and sp^3/sp^2 content [7]. It is well known that film thickness has significant influence on the mechanical properties, tribology properties and electrical properties as well as corrosion properties. In addition, the many defects (pinholes, cracks, and scratches) on the surface as initiating point induced to redox reaction that accelerates corrosion. The corrosion severity normally depends on an aqueous solution containing types of aggressive ions, i.e., chloride ion (Cl^-), hydrogen ion (H^+), and hydroxide ion (OH^-). Those ions are absorbed at the surface of the a-C:H film, then penetrate and attack the thin films resulting in corrosion at surface [8]. More researches [8], [9] clarify that the a-C:H films provide good corrosion resistance for engineering parts. However, a part of engineering is still focused on the thickness of coating to protect the surface of substrate, which considered both the mechanical and corrosion properties.

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II. EXPERIMENTAL

A. Sample Preparation and Deposition

The p-type Si (100) oriented wafer were used as substrates. The substrates were cleaned with an acetone and subsequent ethanol and distilled water in an ultra-sonic bath each for 30 min and then dried in air. Prior to deposition, the substrates were etched by low energy argon ions (Ar^-) to remove the native oxide such as silicon dioxide (SiO_2) on the surface with negative bias voltage at 0.3 kV for 10 min. For deposition process, the main chamber is pumped by the rotary and turbo molecular pumps to vacuum as base pressure at ~2.0 \times 10^{-3} \text{ Pa}. And then, the precursors were feed to main chamber where the flow rate of precursors were controlled by mass flow controller i.e., 15 sccm of argon gas (Ar), 15 sccm of hydrogen gas (H_2), and 25 sccm of benzene (C_6H_6). The substrates were deposited with a-C:H films for 1, 3, 5, 7, and 10 min deposition times.
with 0.5 kV negative bias voltage and 13.56 MHz rf-oscillator by the rf-PECVD technique.

B. Characterization of Films

The true density and thickness of films were characterized by XRR method (M03XHFMXP3, Mac science). The XRR data was obtained using CuKα radiation (λ = 1.54 Å). The fitting of the XRR data to simulated curves, was performed using GXRR software. In addition, the bonding structure of the a-C:H films were characterized by Raman spectroscopy with 514.5 nm produced by a 20 mW of Ar-laser ion as the excitation source in the range of 1000-2000 cm⁻¹. The Raman spectra were curve fitted with two Gaussian functions by OriginPro8.5 software to evaluate the intensity I₉/I₀ and the D- and G-bands position.

C. Mechanical Test

Mechanical properties of samples, i.e., hardness and elastic modulus were measured using a Fischer H-100 pico-indentation hardness tester which is suitable for the diamond-like carbon or amorphous carbon films. For the hardness testing, sixteen indents were performed on each sample using the diamond Vicker tip and the average value of the hardness was calculated. The hardness and elastic modulus of each indent were determined based on the Oliver and Pharr method [11]; the ultralow load applied was 3 mN. Moreover, the loading and unloading rate was 0.003 mN/s set to be constant throughout the measurement. The indenter was moderately moved with a speed of 0.1 nm/s and its pause at maximum load was 5 s. This technique was used in this study because it eliminates any influence from the substrate on the resulting measurement.

D. Corrosion Test

Corrosion properties of Si (100) substrate and a-C:H films deposited on Si-substrates were carried out by electrochemical technique in air-saturated 3.5 wt.% NaCl solution with pH 2 at room temperature in accordance with ASTM standard G44-99 [12]. The polarization measurements were performed using an Autolab PGSTAT 302H. A three electrode cell was used for the polarization measurement; a saturated silver chloride electrode (Ag/AgCl with 3.0 M KCl) was employed as the reference electrode, graphite was used as the counter electrode and the bare sample and the deposited a-C:H films were the working electrode. The fresh aqueous solution of 3.5 wt.% NaCl was prepared for this experiment the same as seawater. The pH of the NaCl solution was approximately 6.28 after fresh preparation that was adjusted to acid (pH 2) by adding droplets of hydrochloric acid (HCl). In this study, all samples were allowed to stabilize at open circuit potential (OCP) for 4 min. The potential measurements were carried out from 150 mV to 2500 mV with a scan rate of 1.0 mV/s. An exposed surface area of all samples (working electrode) was fixed to 0.28 cm². The corrosion rate was calculated from the polarization curve according to Faraday’s law, and was estimated by the Tafel extrapolation method [13]. Moreover, the protective efficiency (Pₚ) of films was determined by using Icorr value [14]. Finally, the field-emission scanning electron microscopy (FE-SEM) has been used to study the surface of the uncorroded and corroded areas of a-C:H films.

III. RESULTS AND DISCUSSION

A. Characterization of Films

The physical properties of our films are summarized in Table I, as characterized on the surface by XRR method. In our results, it was found that the thickness of films depend on the deposition time of the process. The true density of the film was calculated by fitting the XRR curves with GXRR software following the Parrat’s Method [15]. The true density of A, B, C, D, and E samples are in the range of 1.50-1.98 g/cm³ such as with [5], [16], whereas the D and E samples kept the lowest and highest for the true density. The surface roughness of a-C:H films was in the range of 0.11-0.57 nm. Moreover, B. Bruno’s group had reported the thickness, density and surface roughness of the films to be related to the mechanical properties i.e., hardness, elastic modulus etc. However, some research showed how the sp³ content arise with higher thicknesses for a-C:H films corresponding to the density [5].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition time (min)</th>
<th>Thickness (nm)</th>
<th>Density (g/cm³)</th>
<th>Surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>-</td>
<td>-</td>
<td>2.55</td>
<td>0.50</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>47</td>
<td>1.82</td>
<td>0.34</td>
</tr>
<tr>
<td>B</td>
<td>3</td>
<td>90</td>
<td>1.84</td>
<td>0.49</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>350</td>
<td>1.83</td>
<td>0.11</td>
</tr>
<tr>
<td>D</td>
<td>7</td>
<td>600</td>
<td>1.50</td>
<td>0.34</td>
</tr>
<tr>
<td>E</td>
<td>10</td>
<td>900</td>
<td>1.98</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Raman spectroscopy is performed to characterize the a-C:H film due to its ability to distinguish bonding type and domain size [17]. The a-C:H films consist of a mixture of both sp² and sp³ coordinated carbon regions as well as hydrogen [5]. The sp² site of disorder band designated as “D-band” (1200-1450 cm⁻¹) and C sp³ site of microdomains designated as “G-band” (1580-1600 cm⁻¹). The sp² site is a possibility that formed the small clusters in the matrix of the a-C:H films and sp³ sites are bonded to more hydrogen until eventually saturated [5], [18]. Figs. 1 (a) to (e) show the asymmetric shape of diamond-like carbon peaks in the range of 1000-2000 cm⁻¹, representing the characteristics of a-C:H films [19]; two typical features were detected, a D-band centered around 1374-1391 cm⁻¹ and G-band centered around 1571-1577 cm⁻¹. The intensity of the I₉/I₀ ratio was integrated in the area under curve of D- and G-bands that involved sp³/sp² contents in the films. The sp³/sp² content in the a-C:H films cannot be calculated directly from Raman spectra but can be estimated from the fitting as the position using the full width at half maximum (FWHM) of D- and G-bands, corresponds to the I₉/I₀ ratio [20]. A growing I₉/I₀ ratio is related to an increase of graphite-like nanocrystallines [21].

The FWHM of each G-band sample were 180, 183, 180, 175, and 185 cm⁻¹, respectively. The E sample with 900 nm
thickness shows the highest FWHM, revealing the internal stress into the film due to the \(sp^3\) carbon domain at around the \(sp^2\) site [19]. Hence, the D- and G-band widths showed that the \(sp^3\) content in the films control the mechanical properties i.e., hardness, elastic modulus and internal stress.

It is clear that in Fig. 2, the G-band was an indicator of the increasing thickness as the G-band shifted towards higher wave numbers from 1571-1577 cm\(^{-1}\). In the same way, the D-band also shifted towards higher wave numbers. The shifting of G-band toward higher wave number is related to the increase of \(sp^3\) content in the a-C:H films due to the ion carbon implantation into the film layer during deposition that was formed by C-C bonding in the films as reported in [5], [19]. In addition, the E sample showed the lowest intensity \( I_D/I_G \) ratio, this indicates that the a-C:H films presented an increase of \(sp^3\) content. The D-band displayed vibration of \(sp^2\) atoms in aromatic rings (hexagonal), which indicated disorder of bond angle due to the disappearance of the long range translation symmetry of polycrystalline graphite and amorphous carbon films, while G-band corresponds to C-C bond stretching vibration of all pairs of \(sp^2\) atoms in both ring and chains of graphite layer for single crystalline graphite structure [5], [22]. Furthermore, higher \(sp^3\) content can be achieved by applying negative bias voltage of 0.5 kV, resulting in higher density and better mechanical properties [23]. However, it is not only the effect of thickness but also the effect of hydrogen atoms bonded with amorphous carbon film as reported in [5], [10]. In this paper, the hydrogen (H) content in these a-C:H films were calculated by simple formula according to [17], which is a qualitative analysis. The H contents are in the range of 31-35% that is the intermediate H content in the a-C:H films.

**Fig. 2 Relationship of film thicknesses, G-positions and intensity \(I_D/I_G\) ratio for a-C:H films deposited by rf-PECVD technique**

**B. Mechanical Properties**

Fig. 3 (a) illustrates the loading and unloading displacement depth curves obtained by pico-indentation of the a-C:H films deposited on Si-substrate with various thicknesses at maximum ultralow-load up to 3 mN. The graphs show a good reproducibility of the pico-indentation test. As the displacement depth curves, depending on the thickness of the a-C:H films, the deposited samples can be classified in two groups as soft- and hard-amorphous carbons. In particular, the D sample was a soft a-C:H film because it kept both its low density and hardness. It can be implied that some areas in/on layer of the a-C:H films included defects such as pinholes, delamination and compound contaminations which occurred during the deposition process [24]. The A, B, C, and E samples were hard a-C:H films because of their dense and homogenous matrix, which is revealed against the indentation force or compressive force. The penetration depth values of soft material are 112 nm and hard-material is in the range of 86-91 nm. As mentioned above, the results of displacement depth curves correlated to the amount of \(sp^2\) site arising into the a-C:H films as also described in part of Raman spectra characterization. However, these results show good agreement with other works [8], [23].

All indentation behaviors of the samples were investigated by pico-indentation as shown in Fig. 3 (b), which shows the hardness and elastic modulus values of the a-C:H films at different thicknesses. The hardness values of all samples are 13.5, 15.3, 15.0, 9.5, and 18.7 GPa respectively. It is obvious that the E sample had a higher hardness than the A, B, C, and D samples. This is because of the effects of thickness and density increasing in the a-C:H films [19]. Therefore, it has the ability to resist compressive force from indented tip. In contrast, the D sample has a lowest hardness with 600 nm of thickness due to the film having defects that affected the matrix as non-homogenous. In addition, the elastic modulus was determined.
to support the result of hardness values. It is clear that all elastic modulus of samples is directly proportional to the hardness. The elastic modulus of A, B, C, and E samples is in the range of 127-143 GPa, which is an indicative of the α-C:H films being hard-materials. D sample, however, kept the elastic modulus about 96 GPa as soft-materials. Above all, the E sample prepared with 900 nm thickness for 10 min of deposition time, represents the highest hardness property, whereas the D sample shows the lowest hardness property.

C. Corrosion Properties

The corrosion properties in terms of polarization curves are shown in Fig. 4. It is clear that the behavior of polarization curve of Si-substrate (bare sample) and α-C:H films were deposited on Si-substrate samples in air-saturated 3.5 wt.% NaCl solution for pH 2 at room temperature. The polarization curve consists of the anodic and cathodic lines, which intersects and gives formation to the $E_{corr}$ and $I_{corr}$. It can be indicated that the corrosion behavior of all samples were changed with various thicknesses. An improvement of the α-C:H films deposited on Si-substrate showed that the current density of polarization curves were shift toward lower than the bare sample. This shows that α-C:H films had the ability to enhance corrosion resistance. Besides, it was found that the passive region was formed of all the α-C:H films especially the E sample with 900 nm thickness was excellent passive film, with low current density. In addition, a point to be noted is the anodic line of polarization curves that there is noise due to effect from Cl\(^{-}\) in aggressive acid solution (at pH 2) as reported in [25]. The information from polarization curve is not only described as corrosion behavior but also shows data about the protective efficiency of films [14].

![Fig. 3](image1.png)

![Fig. 4](image2.png)
The a-C:H films were successfully deposited on Si substrate with different thicknesses with 0.5 kV of intermittently negative bias voltage by rf-PECVD. The influence of different thickness affected the physical properties in terms of the true density and surface roughness changed. The a-C:H films were included with sp² and sp³ hybridized into amorphous carbon films. The intensity $I_{sp}/I_{sp}$ ratio variation to $sp^3$ content in the G-band, revealed the $sp^3$ content arise in the a-C:H films. The G-band’s peak position tends to increase when the thickness increased. In mechanical properties, the high true density films presented high hardness values; it possessed the ability to resist compressive force which is related to $I_{sp}/I_{sp}$ ratio decreases. The a-C:H films were classified as hard (A, B, C, and E samples) and soft (D sample) amorphous carbon materials. In addition, the elastic modulus was indicated to the stiffness property of the a-C:H films. As corrosion properties, the a-C:H films show enhanced corrosion resistance and high protective efficiency controlled by small $sp^3$ clusters in amorphous carbon films. Lastly, the FE-SEM images show corrosion type of a-C:H films as the localized corrosion.

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REFERENCES


IV. CONCLUSION

Table II

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (µA/cm²)</th>
<th>$R_{anony}$ (mm/year)</th>
<th>$P_i$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>475</td>
<td>$6.35 \times 10^3$</td>
<td>$5.72 \times 10^{-7}$</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>190</td>
<td>$0.19 \times 10^3$</td>
<td>$6.08 \times 10^{-7}$</td>
<td>97.00</td>
</tr>
<tr>
<td>B</td>
<td>217</td>
<td>$0.12 \times 10^3$</td>
<td>$3.61 \times 10^{-7}$</td>
<td>98.11</td>
</tr>
<tr>
<td>C</td>
<td>291</td>
<td>$0.11 \times 10^3$</td>
<td>$3.54 \times 10^{-7}$</td>
<td>98.27</td>
</tr>
<tr>
<td>D</td>
<td>213</td>
<td>$0.74 \times 10^3$</td>
<td>$2.86 \times 10^{-5}$</td>
<td>88.35</td>
</tr>
<tr>
<td>E</td>
<td>137</td>
<td>$0.07 \times 10^3$</td>
<td>$2.10 \times 10^{-7}$</td>
<td>98.90</td>
</tr>
</tbody>
</table>

Fig. 5 shows the surface FE-SEM images of corroded areas of E sample before and after corrosion test. The D sample was selected for this study because of its high corrosion rate and extremely corrosive, shows the characteristic of corrosion form. However, it is well known that the a-C:H film has a rather smooth surface although there are some regions considered as weakness points such as pinhole, delamination and scratch trace (Fig. 5 (a)), which easily absorbed with the several aggressive ions in the solution such as $H^+$, $Cl^-$, and $OH^-$ [26]. In addition, the $Cl^-$ ions absorbs on the locally surface then replacing the $OH^-$ and decrease the surface stability of the a-C:H films [25]. Furthermore, when the films had initiation crack, those ions will intensely attack at the surface and penetrate into the film, and then it induces the “pit”, as a form of extremely localized corrosion that leads to the creation of small holes onto/into the a-C:H films. The pits were usually generated near the defects (Fig. 5 (b)). The pit size was estimated from FE-SEM image as approximately in range of 0.5-2.0 μm. However, it is obvious that different thickness of films had effected to corrosion properties i.e., $E_{corr}$, $I_{corr}$, and corrosion rate.

Fig. 5 Surface FE-SEM images of a-C:H film (D sample) before (a) and after (b) corrosion test in air-saturated 3.5 wt.% NaCl solution for pH 2 at room temperature.
S. Tumnee was born on November 5, 1985 in Thailand. He received his bachelor and master degrees of engineering in Metallurgical Engineering from Suranaree University of Technology, Nakhon Ratchasima, Thailand in 2009 and 2012, respectively. He was an assistant researcher at Beamline 3.2B, Synchronrotron Light Research Institute (SLRI), Thailand in 2009-2013. He is a currently studying Ph.D. degree in the Department of Materials Science and Technology, Nagaoka University of Technology, Japan. His research interest focused on synthesis and characterization of diamond-like carbon films by sputtering and PECVD technique. He is a postdoctoral fellow at Nagaoka University of Technology, Japan at the Department of Materials Science and Technology. Prof. Hidetoshi Saitoh is the head of research group of Corrosion and Surface Technology. His research interest focused on surface-plasmon resonance (SPR) of diamond-like carbon films.

P. Wongpanya received her doctoral degree from University of the Federal Armed Forces Hamburg, Germany in 2008. She is an Assistant Professor in School of Metallurgical Engineering in 2010. Assist. Prof. Pornwasa Wongpanya’s research has been published in corrosion science journals and international conferences. Her research interest focused in the field of numerical simulation of welded component, corrosion of metals, thin-films, and surface technology.

I. Toda was born on July 24, 1981 in Japan. He received his doctoral degree from Nagaoka University of Technology in 2010. He was a postdoctoral research fellow in Nagaoka University of Technology, Japan at the Department of Materials Science and Technology. Dr. Ikumi Toda is the head of research group of Corrosion and Surface Technology. She is a professor in the Department of Materials Science and Technology at Nagaoka University of Technology. Her work focuses on synthesis of diamond-like carbon films by plasma enhanced chemical vapor deposition (PECVD) technique.

Y. Nakaya was born on August 20, 1990 in Japan. He received his bachelor degree from Nagaoka University of Technology. He is currently a master’s degree student of the Department of Materials Science and Technology at Nagaoka University of Technology. His research focuses on surface-plasmon resonance (SPR) of diamond-like carbon films.

N. Kockhunthot was born on June 3, 1998 in Thailand. He received his bachelor (2nd honors) and master degrees of engineering in Metallurgical Engineering from Suranaree University of Technology. He is currently a doctor student of the School of Metallurgical Engineering at Suranaree University of Technology. His research focuses on Diamond-like carbon films deposited on the hot-worked tool steel by filtered cathodic vacuum arc technique.

S. Arakawa was born on October 24, 1991 in Japan. He received his bachelor degree from Nagaoka University of Technology. He is currently a master’s degree student of the Department of Materials Science and Technology at Nagaoka University of Technology. His work focuses on electrochemical impedance of diamond-like carbon films.

H. Saitoh received his doctoral degree from Nagaoka University of Technology in 1990. He joined Materials Research Laboratory of the Pennsylvania State University as a research associate in 1990. He moved to Ibaraki University in 1992. He became an associate professor in 1994 and a full professor in 2003 at Nagaoka University of Technology. He has been serving as the Project Leader of the NEDO-METI Japan International Standardization Program for diamond-like carbon films in the year of 2006 and 2009-2011. Prof. Hidetoshi Saitoh is the head of the Opto-Electronic Ceramics laboratory which included the carbon materials and oxide materials.