

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

S. Tunmee, P. Wongpanya, I. Toda, X. L. Zhou, Y. Nakaya, N. Konkunthot, S. Arakawa, H. Saitoh

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 arise at different thicknesses of the *a*-C:H films. In terms of mechanical properties, the high hardness and elastic modulus values showed the elastic and plastic deformation behaviors related to sp^3 content in amorphous carbon films. Electrochemical properties showed that the *a*-C:H films exhibited excellent corrosion resistance in air-saturated 3.5 wt.% NaCl solution for pH 2 at room temperature. Thickness increasing affected the small sp^2 clusters in matrix, restricting the velocity transfer and exchange of electrons. The deposited *a*-C:H films exhibited excellent mechanical properties and corrosion resistance.

Keywords—Thickness, Mechanical properties, Electrochemical corrosion properties, *a*-C:H film.

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 adsorbed 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 potentiodynamic 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.

II. EXPERIMENTAL

A. Sample Preparation and Deposition

The *p*-type Si (100) orientated 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 $\sim 2.0 \times 10^{-3}$ 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

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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 $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). 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-ion laser 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 I_D/I_G ratio 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 cm^2 . 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 (P_i) of films was determined by using I_{corr} 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/cm^3 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 sp^3 content arise with higher thicknesses for *a*-C:H films corresponding to the density [5].

TABLE I
PHYSICAL PROPERTIES OF HYDROGENATED AMORPHOUS CARBON FILMS

Sample	Deposition time (min)	Physical properties		
		Thickness (nm)	Density (g/cm^3)	Surface roughness (nm)
Si	-	-	2.55	0.50
A	1	47	1.82	0.34
B	3	90	1.84	0.49
C	5	350	1.83	0.11
D	7	600	1.50	0.34
E	10	900	1.98	0.57

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 sp^2 and sp^3 coordinated carbon regions as well as hydrogen [5]. The sp^2 site of disorder band designated as "D-band" (1200-1450 cm^{-1}) and sp^3 site of microdomains designated as "G-band" (1580-1600 cm^{-1}). The sp^2 site is a possibility that formed the small clusters in the matrix of the *a*-C:H films and sp^3 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 I_D/I_G ratios was integrated in the area under curve of D- and G-bands that involved sp^3/sp^2 contents in the films. The sp^3/sp^2 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 I_D/I_G ratio [20]. A growing I_D/I_G 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.

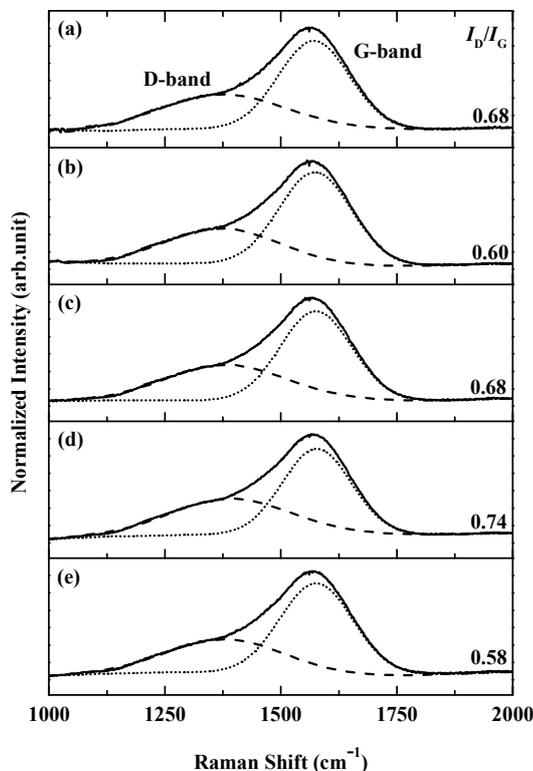


Fig. 1 Raman spectra of a -C:H films deposited on the Si (100) substrate at different thicknesses; (a) A sample (47 nm), (b) B sample (90 nm), (c) C sample (350 nm), (d) D sample (600 nm), and (e) E sample (900 nm)

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.

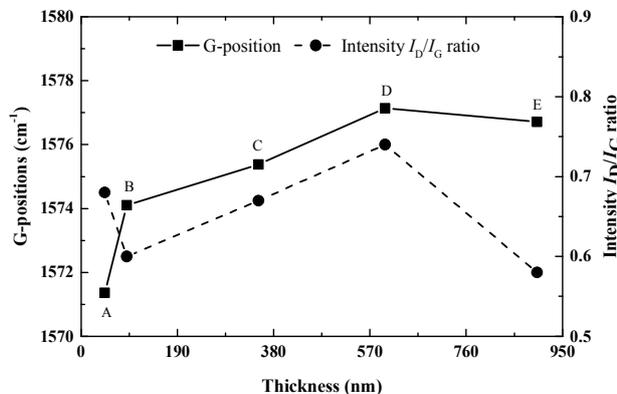


Fig. 2 Relationship of film thicknesses, G-positions and intensity I_D/I_G ratio for a -C:H films deposited by rf-PECVD technique

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^3 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 *a*-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.

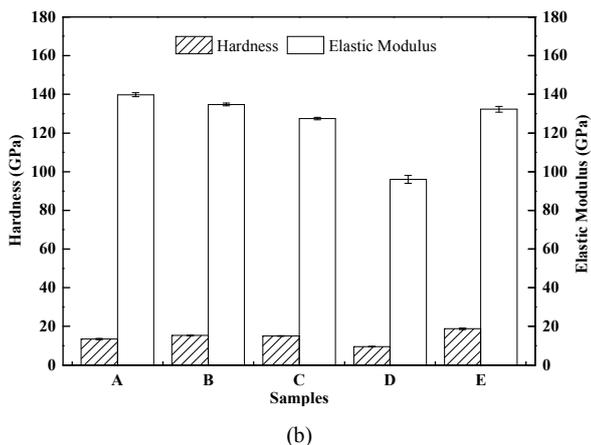
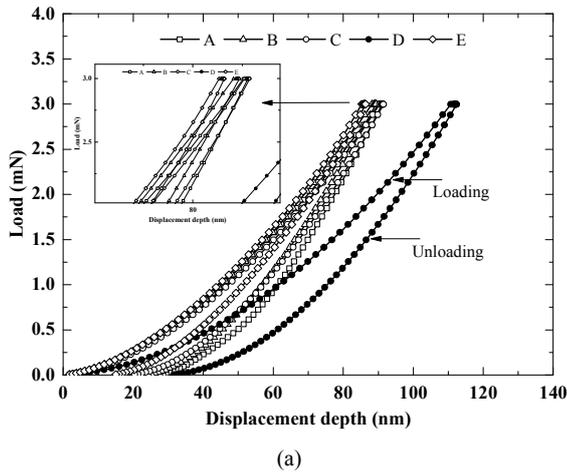


Fig. 3 Mechanical properties of *a*-C:H films were obtained by pico-indentation with maximum ultralow-load employed 3 mN; (a) the loading and unloading displacement depth curves, (b) the hardness and elastic modulus with different thicknesses

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 *a*-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 *a*-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 *a*-C:H films had the ability to enhance corrosion resistance. Besides, it was found that the passive region was formed of all the *a*-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].

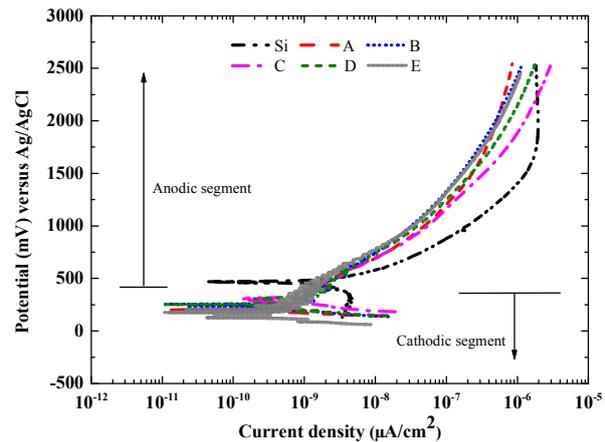


Fig. 4 Potentiodynamic polarization curves of the Si-substrate (bare sample) and *a*-C:H films deposited on Si-substrate in air-saturated 3.5 wt.% NaCl solution for pH 2 at room temperature

Electrochemical parameters of all samples were presented in Table II. The E_{corr} of *a*-C:H films is in the range of 137-291 mV, indicated to high society (or noble) materials. In contrast, the bare sample shows the I_{corr} higher than other samples, that the corrosion rate of bare sample was higher than all *a*-C:H films. Besides, the soft *a*-C:H films sample had protective efficiency around 88.35 % where the hard *a*-C:H films was in range the 97.00-98.90%. It might be said that the performance of soft and hard *a*-C:H films are the ability and durability under condition of 3.5 wt.% NaCl solution for pH 2 at room temperature of applications. Thus, it implied that the *a*-C:H films were an excellent protective films on corrosion resistance with different thicknesses. However, the corrosion resistance and protective efficiency of *a*-C:H films corresponded to I_D/I_G ratio decreases, revealed the small sp^2 clusters in matrix, and restricted the transfer velocity and exchange of electrons [8]. This reason shows that the *a*-C:H films are able to resist severe environment.

TABLE II
ELECTROCHEMICAL PROPERTIES OF SAMPLES

Samples	Electrochemical properties			
	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	R_{mp} (mm/year)	P_i (%)
Si	475	6.35×10^{-3}	5.72×10^{-5}	-
A	190	0.19×10^{-3}	6.08×10^{-7}	97.00
B	217	0.12×10^{-3}	3.61×10^{-7}	98.11
C	291	0.11×10^{-3}	3.54×10^{-7}	98.27
D	213	0.74×10^{-3}	2.86×10^{-6}	88.35
E	137	0.07×10^{-3}	2.10×10^{-7}	98.90

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 absorb 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.

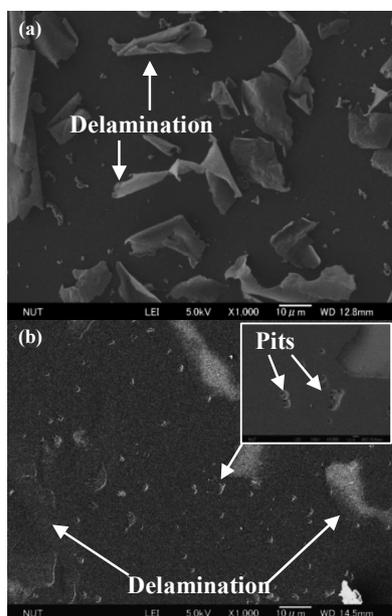


Fig. 5 Surface FE-SEM images of *a*-C:H film (D sample) before (a) and after (b) corrosion test in air-saturated 3.5 wt.% NaCl solution for pH 2 at room temperature

IV. CONCLUSION

The *a*-C:H films were successfully deposited on Si substrate with different thicknesses with 0.5 kV of intermediately 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 sp^2 and sp^3 hybridized into amorphous carbon films. The intensity I_D/I_G 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_D/I_G 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^2 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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