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The Effects of Applied Negative Bias Voltage on Structure and Optical Properties of *a*-C:H Films

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***Abstract*—**Hydrogenated amorphous carbon (*a*-C:H) films have been synthesized by a radio frequency plasma enhanced chemical vapor deposition (rf-PECVD) technique with different bias voltage from 0.0 to -0.5 kV. The Raman spectra displayed the polymer-like hydrogenated amorphous carbon (PLCH) film with 0.0 to -0.1 and *a*-C:H films with -0.2 to -0.5 kV of bias voltages. The surface chemical information of all films were studied by X-ray photoelectron spectroscopy (XPS) technique, presented to C-C (sp^2 and sp^3) and C-O bonds, and relative carbon (C) and oxygen (O) atomics contents. The O contamination had affected on structure and optical properties. The true density of PLCH and *a*-C:H films were characterized by X-ray refractivity (XRR) method, showed the result as in the range of 1.16-1.73 g/cm^3 that depending on an increasing of bias voltage. The hardness was proportional to the true density of films. In addition, the optical properties i.e. refractive index (n) and extinction coefficient (k) of these films were determined by a spectroscopic ellipsometry (SE) method that give formation to in 1.62-2.10 (n) and 0.04-0.15 (k) respectively. These results indicated that the optical properties confirmed the Raman results as presenting the structure changed with applied bias voltage increased.

***Keywords*—**Negative bias voltage, *a*-C:H film, Oxygen contamination, Optical properties.

I. INTRODUCTION

DIAMOND-LIKE carbon (DLC) films are being widely studied in several research fields such as electrical, mechanical, tribology, chemical inertness, structural, and optical properties [1]-[3]. One of the most popular is the hydrogenated amorphous carbon (*a*-C:H) film. Category and quality of DLC films depend on the each technique especially the plasma-enhanced chemical-vapor-deposition (PECVD) technique which is the one of the most popular techniques for producing the good quality *a*-C:H films [4]. In the last four decades, the number of publications on DLC films has been continuously increased and important for industrial applications such as automotive parts, biomedical components, cutting tools, and electricity devices [1]-[5]. Recently, the both structure and optical properties of *a*-C:H films were significantly interested [5], [6].

It is well known that the DLC films have several types, e.g., amorphous carbon (*a*-C), hydrogenated amorphous carbon (*a*-C:H), tetrahedral amorphous carbon (*ta*-C), and hydrogenated tetrahedral amorphous carbon (*ta*-C:H) [7]. Here the *a*-C:H films were studied, including the sp^2 and sp^3 hybridized in the matrix which these structures were applied instead of the graphite and diamond forms [8]. There are a few researches purposed the information which applying to bias voltage at substrate affected the structure of film changed [9], [10] as well as mechanical and optical properties [11], [12]. In addition, the mechanical properties are related to the density and amount of sp^3 site in amorphous carbon films [13]. The optical properties were high potential studied on the subject of the relationship between the structure and optical constants i.e., refractive index (n) and extinction coefficient (k) of the *a*-C:H films [13]-[15]. The n may be changed between 1.8-2.4 for the *a*-C:H films whereas the PLCH films had the value less than 1.8 [16]. However, very few researches have studies on the effect of bias voltage on the structure and optical properties of the *a*-C:H films deposited by rf-PECVD technique at room temperature for application, which expected to result good potential for commercialization.

This study is focused on the influence of applied negative bias in the range of 0.0-0.5 kV (low-intermediately of bias voltage) at substrate on the structure, density, hardness, and optical constants of *a*-C:H films deposited on the Si-substrate. The Raman spectroscopy is a standard analysis method for the characterization of amorphous carbon films which estimated to cover the D- and G-bands of spectra. The structural analysis usually relates to finding out the intensity ratio (I_D/I_G) of the D- and G-bands. In addition, the X-ray photoelectron spectroscopy (XPS) was used to gain an insight on surface chemical, structure and bonding of these films. The true density and thickness are characterized by the X-ray reflectivity (XRR) method which is a powerful tool for surface sensitivity analysis. The pico-indentation testing was selected for hardness measurement of films. The optical properties of *a*-C:H films were estimated by the spectroscopic ellipsometry (SE). This method is routinely used to determine the film thickness and optical constants for single and multi-layers based on a change in polarization as light interacts with layered materials [17].

II. EXPERIMENTAL

A. Sample Preparation

The substrates in this experiment were *p*-type Si (100) which cut into 10 mm × 10 mm × 0.6 mm size, and ultrasonically cleaned in distilled water, acetone and ethanol solutions. Before deposition, the substrates were sputter cleaned by argon ion (Ar$^+$) to remove native oxide on the surface with self-bias voltage at 0.3 kV for 10 min. Subsequently, the chamber was pumped by a rotary and turbo molecular pumps to base pressure at 2 × 10^{-2} mbar. The hydrogenated amorphous carbon (*a*-C:H)

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films were grown on Si-substrate by the rf-PECVD technique with 13.56 MHz oscillator and negative bias voltage was varied from 0.0 to 0.5 kV in the pulsed for 15 min deposition time for each sample. Furthermore, the deposited *a*-C:H films were carried out using a precursor gas mixture of argon gas (Ar), hydrogen gas (H_2), and benzene (C_6H_6) as 15:15:20 sccm which controlled by mass flow controller (MFC). Finally, the schematic diagram of the rf-PECVD process for this experiment was received as shown in Fig. 1.

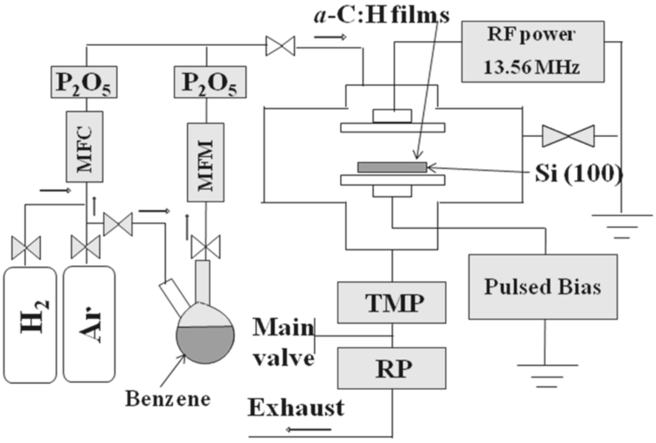

Fig. 1 Schematic diagram of the rf-PECVD process

B. Surface Characterization and Hardness Test

The bonding structure of the *a*-C:H films were characterized by a Raman spectroscopy with 514.5 nm produced by a 10 mW of Ar-ion laser as the excitation source in the range of 1000-2000 cm^{-1}. The Raman spectra were fitted with two Gaussian functions by OriginPro 8.5 software to estimate the I_D/I_G ratio and the shifting of D- and G- peaks position. The surface chemical information was characterized by XPS technique (JEOL, JPS-9010TR), using Al*Kα* radiation in fixed analyzer transmission mode; the measurement was controlled with 20 eV of pass energy, 0.1 eV step size, and 100 eV of Dwell time. The peaks of XPS spectra were fitted with Gaussian and Lorentzian functions and background was subtracted by Shirley method at different negative bias voltage. In addition, the thickness and true density were investigated by the X-ray reflectivity (XRR) method M03XHFMXP3, Mac science) by using a Cu*Kα* X-ray source (1.54 Å of wave length) under the conditions of a scan rage of 0.184-2.500° and 0.004° of step size.

The hardness test was obtained by a pico-indentation tester (FISCHER H-100) which is the high powerful tools for hardness measurement. For this experiment, the ultralow load applied to sample with 3 mN, the loading and unloading rate was 0.003 mN/s set to make the experiment constant and the indenter moved at 0.1 nm/s of speed.

C. Optical Properties Test

The optical properties in terms of the refractive index (n) and extinction coefficient (k) of the *a*-C:H films were determined by SE method (HORIBA, Jobin Yvon, UVISEL 23301010I). The SE which is a rapid and powerful for non-destructive technique was used to characterize thin films. The angle of incidence was set to 70°, with using the rotating compensator ellipsometer on an ex-situ experiment. Data were fitted by multi-layers Tauc-Lorentz model, which were considered with χ^2 in order to eliminate the error from angle of incidence. In this case, the authors had designed the model for data fitting which contained the first Si-substrate, a second silicon dioxide (SiO_2) layer, and a third *a*-C:H film mixing with 50% of voids.

III. RESULTS AND DISCUSSION

A. Surface Characterization and Hardness

Fig. 2 shows the Raman spectra of the PLCH film and *a*-C:H films deposited on Si-substrate with different negative bias voltages. The initial bias voltage set to be 0.0 kV and 0.1 kV without the peak signal of the *a*-C:H films as shown in Figs. 2 (a)-(b). This feature is similar to the PLCH film as reported in [18], [19]. In contrast, the bias voltage in the range of -0.2 to -0.5 kV presented the typical features of the *a*-C:H films which consists of the D- and G-bands in the range of 1000-2000 cm^{-1} [20] as shown in Figs. 2 (c)-(f). The centres of D- and G-bands were around 1374-1391 cm^{-1} and 1571-1577 cm^{-1}, respectively. Moreover, as applied negative bias voltage at substrate affected to the G-band's position shifted towards higher wave number from 1556 to 1596 cm^{-1}. The I_D/I_G ratio had decreased from 1.23 to 0.71 with increasing the bias voltage from -0.2 to -0.5 kV. This reason might indicated the sp^3 site in matrix increased [20]-[22], related to both resulting of the density and hardness.

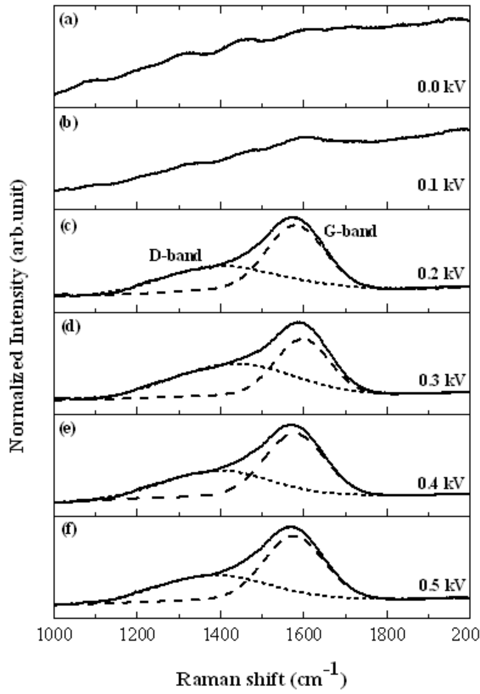

Fig. 2 Raman spectra of the PLCH and *a*-C:H films deposited on Si-substrate with different negative bias voltages

Note that the XPS technique is a good tool for surface sensitive analysis, which gives details of qualitative and quantitative of chemical information [23], [24]. It is clear that from Fig. 3, the XPS spectra show the C *1s* peak of the *a*-C:H films with different negative bias voltages. The behavior of C *1s* peaks had shifted to higher binding energy with increasing of bias voltage; this is reason why oxidation state of *a*-C:H films had changed. The C *1s* peak of XPS spectra deconvoluted the three peaks at around 284.0, 285.0, and 287.5 eV [24], [25]. The strong peaks at 284.0 and 285.0 eV are corresponded to C-C sp^2 (graphite) and C-C sp^3 (diamond) bonds into *a*-C:H films while the weak peak at 287.5 eV is corresponded to C-O bonding which supposed to contamination from precursor, deposition process, moisture in atmospheric, and sample preparation. It indicated that the O contamination on surface and applied bias voltage at the substrate affected to shifting of binding energy increased [24], [26]; it implied that the diamond-like (sp^3) structure in matrix increased.

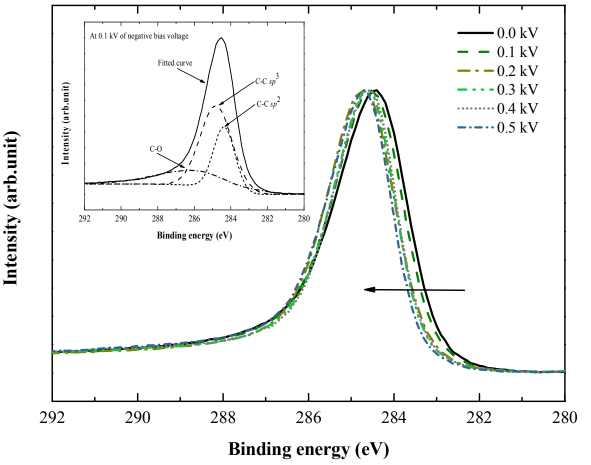

Fig. 3 XPS spectra of C *1s* peak of all samples prepared at different negative bias voltages

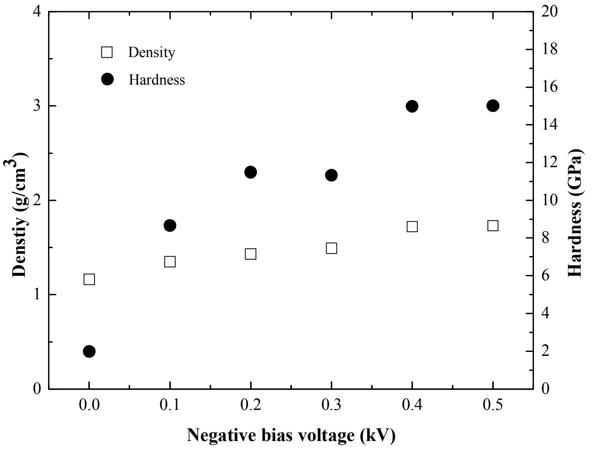

Fig. 4 The true density and hardness of the PLCH and *a*-C:H films at the different bias voltages

The surface chemical quantitative analysis indicates that relative atomic C (C-C sp^2 and sp^3) and O contents as presented in Table I. The total relative atomic contents of C-C bonding in C *1s* peaks were calculated which combined two structure i.e., sp^2 and sp^3 hybridized. It revealed that the relative C atomic contents were high as in the range of 88-98 at.% while an increasing of negative bias voltage affected to the relative O atomic contents gradually decreased as supported by [26], as in the range 1-12 at.%, related to shifting of binding energy. However, the *a*-C:H films were easily contaminated with O atoms in atmosphere. It had influenced on optical properties especially the *n* value as reported in [27]. As results, it also implied that at 0.5 kV of bias voltage is an alternative choice for growing of good *a*-C:H films which is low O contamination.

TABLE I
SURFACE CHEMICAL INFORMATION OF ALL FILMS

Negative bias voltage (kV)	Chemical information	
	Peaks	Relative atomic contents (at.%)
0.0	C-C (sp^2 and sp^3)	91
	C-O	9
0.1	C-C (sp^2 and sp^3)	88
	C-O	12
0.2	C-C (sp^2 and sp^3)	89
	C-O	11
0.3	C-C (sp^2 and sp^3)	93
	C-O	7
0.4	C-C (sp^2 and sp^3)	96
	C-O	4
0.5	C-C (sp^2 and sp^3)	98
	C-O	2

As can be seen from Fig. 4, the hardness results showed good agreement with the true density of the films. It was found that the both hardness and density values arise with applied negative bias voltage increase, however, the hardness values of the *a*-C:H films are in the range of 11-15 GPa that showed the hard *a*-C:H films while the density of *a*-C:H films are in the range of 1.43-1.73 g/cm^3. Besides, the hardness and density of PLCH films are less than 8 GPa and 1.35 g/cm^3 respectively. Hence, an applied negative bias voltage at substrate can change PLCH film to DLC film [19] such as *a*-C:H film. Thus, it might be said that the sp^3 site significantly increase into the amorphous carbon film. The sp^3 site as one of variables controlled the mechanical properties such as hardness and elastic modulus of *a*-C:H films [20]. However, it is not only the effect of bias voltage but also the effect of hydrogen (H) contents on the amorphous carbon film, which related to the density and hardness [28].

B. Optical Properties

Fig. 5 shows the refractive index (*n*) and extinction coefficient (*k*) as functions of negative bias voltage. In this article, the *n* is shown to increase from 1.62 (at 0.0 kV) to 2.10 (at -0.5 kV) with the bias an increased, relating to the increasing of density and hardness whereas the relative O atomic contents had significantly decreased [19], [27]. Hence, the *n* is proportional to O atomic contents in *a*-C:H films. Here it was found that the sample without (0.0 kV) and low of bias voltages kept the refractive index lower than 1.8 that gives formation to structure as the PLCH films [16], [19], [29] with exhibit high hydrogen content, low density and low refractive index. In the same way, the *k* values of the PLCH films are less than 0.036;

the light can transmitted through the substrate, or so called transparence materials. Besides, the *k* shows the low values as in the range of 0.12-0.15 with applied bias voltage from -0.2 to -0.5 kV, represented as the *a*-C:H films. This shows that *a*-C:H films had ability in low absorption of light. Even the *k* is directly related to the absorption coefficient (α) and content of sp^2 site decreased in the amorphous carbon films [11], [29]. Therefore, the results of the films at bias voltage -0.3 to -0.5 kV showed the high density and hardness due to the content of sp^2 site decreases.

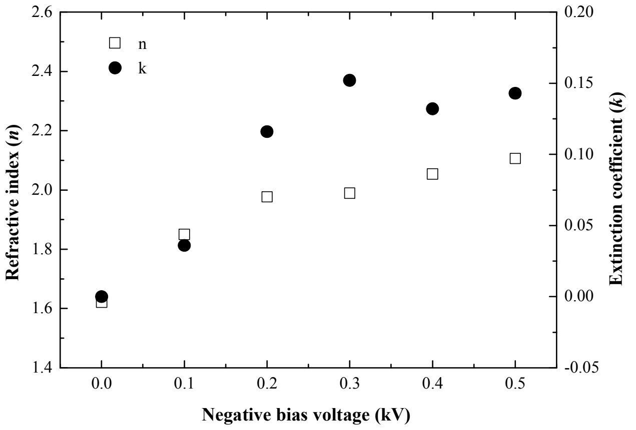

Fig. 5 Optical constants i.e., refractive index (*n*) and extinction coefficient (*k*) of PLCH and *a*-C:H films with 550 nm of wavelength as function with negative bias voltages

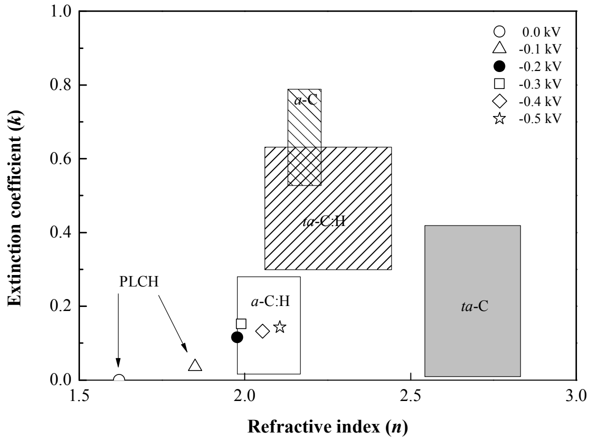

Fig. 6 Correlation of parameters between the structure types and optical constants of PLCH and *a*-C:H films at different negative bias voltage. The region boundaries of each structure types in this figure were modified from [7], [16], [19].

Fig. 6 shows the correlation of parameters between the structure and optical constants. It revealed that the structures of film can be changed by applied bias voltage at substrate in deposition process. Our results presented the two structure types of DLC film i.e., the PLCH and *a*-C:H films. As relationship of the values between *n* and *k* that it can distinguish the type of DLC films, however, the dividing regions of each structure types in Fig. 5 were modified from [7], [16], [19]. In other words, many researches [19], [30] suggested that it is possibility to obtain other types of DLC films such as *a*-C, *ta*-C, and *ta*-C:H by using either other deposition methods or applying other bias voltages. However, the all results also show the great potential for properties in terms of structure, optical constants (*n* and *k*), density as well as hardness for application.

IV. CONCLUSION

The *a*-C:H films were successfully deposited on Si (100) substrate by the rf-PECVD technique using the benzene as precursor. The Raman spectra show the structure of PLCH and *a*-C:H films, which *a*-C:H films deposited contained the two typical feature such as D- and G-bands. The decreasing of I_D/I_G ratio of *a*-C:H films related to the results of the XPS which presented the C-C (sp^2 and sp^3) and C-O (contamination) bonding of C *1s* peak and the relative C and O atomic contents with increasing of negative bias voltage. The correlation of films properties between the true density and hardness increasing in same direction depended on the negative bias voltage. Moreover, the hardness is strongly related to sp^3 site into amorphous carbon films with estimated from the I_D/I_G ratio decreased. For optical properties, the increasing of *n* and *k* depended on the relative atomic O contents and applied bias voltage increased at substrate. These results indicated that the structure had changed from PLCH to *a*-C:H films. Finally, the *a*-C:H film is a good optical transparent materials.

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