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# Deposition of nanometer-thick amorphous carbon films by filtered cathodic vacuum arc under oblique ion incidence conditions

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#### ABSTRACT

Filtered cathodic vacuum arc (FCVA) is a promising technique for synthesizing extremely thin carbon films exhibiting highly tetrahedral  $(sp^3)$  carbon atom hybridization. However, most FCVA studies are for incident ions impinging perpendicular to the substrate surface. In this study, the effects of the ion incidence angle on the thickness, structure, and surface roughness of amorphous carbon (a-C) films deposited under different substrate bias voltages were examined in the light of computational and experimental results. Dynamic simulations and film thickness measurements showed a decrease in film thickness with increasing ion incidence angle, attributed to the decrease in carbon ion fluence on the film surface. Carbon atom hybridization analysis revealed a critical ion incidence angle for a given substrate bias voltage. Simulation and experimental results demonstrated that the enhancement of  $sp^3$  hybridization resulted from carbon-carbon collision cascades on the growing film surface and densification induced by direct and recoil implantation processes controlled by the ion incidence angle and substrate bias voltage. The strong dependence of a-C film growth on the carbon ion incidence angle exemplified by the results of this study has direct implications in the oblique deposition of ultrathin a-C films with predominant tetrahedral carbon atom hybridization. The present study provides a framework for optimizing the ion incidence angle to achieve the deposition of a-C ultrathin films with high  $sp^3$  contents.

# 1. Introduction

Tetrahedral  $(sp^3)$  carbon atom hybridization in amorphous carbon (a-C) films is the primary reason for the exceptional mechanical properties displayed by these films [1-3], making them ideal protective overcoats for numerous applications where preserving the surface integrity is critical to the device functionality and longevity. In particular, high demands for thin-film materials in leading-edge technologies, such as semiconductors, photodiodes, solar cells, miniaturized electromechanical systems, and magnetic storage devices, have generated increased interest in the development of a-C thin films displaying uniformity, ultralow surface roughness, and high hardness.

Among various thin-film deposition methods [4], filtered cathodic vacuum arc (FCVA) is a particularly effective technique for depositing continuous, highly tetrahedral, ultrathin films with excellent mechanical properties [1–7]. An intrinsic feature of FCVA is the development of a plasma comprising energetic ions (e.g.,  $\sim$ 20 eV kinetic energy for C<sup>+</sup> ions [8]), which can be accelerated by applying a negative bias voltage to the substrate. Noteworthy developments of the FCVA technique

aimed to achieve plasma stability and improved efficiency [9-16] led to the growth of a-C films demonstrating good thermal stability [17-19] and exceptional mechanical [11,20,21], tribological [22], and anti-oxidation [23,24] characteristics.

Film deposition by FCVA is a multi-parameter process. Earlier experimental and analytical studies illuminated important effects of key process parameters on the thickness and structure (i.e., type of hybridization) of a-C films. For example, a-C ultrathin films with 50–60 %  $sp^3$  contents were synthesized by FCVA using substrate pulse bias voltages in the range of -25 to -100 V and ion incidence angle equal to  $10^\circ$  measured from the substrate normal [25]. The duty cycle of substrate pulse biasing can also affect the thickness, structure, and surface roughness of FCVA-deposited a-C films [26]. Molecular dynamics (MD) simulations showed that a C<sup>+</sup> ion kinetic energy of 80 eV produced a-C films with the highest density (3.3 g/cm³) and  $sp^3$  content ( $\sim$ 43 %) [27], consistent with the classical subplantation model encompassing the simultaneously occurring processes of shallow subsurface implantation of energetic ions, preferential displacement of atoms with a low displacement energy, and sputtering of weakly bonded atoms [28–30].

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Moreover, MD simulations indicated the existence of a critical ion kinetic energy for growing a-C films with the highest  $sp^3$  content and confirmed that film deposition processes that use energetic particles as film precursors, such as the FCVA method, produce a-C films with a layered structure consisting of an interfacial (intermixing) layer, a bulk layer rich in  $sp^3$  hybridization, and a principally  $sp^2$  hybridized surface layer [31], consistent with the findings of experimental investigations [32,33]. The foregoing studies indicated a strong effect of direct process parameters (e.g., ion incidence angle and substrate bias voltage) and indirect process parameters (e.g., ion kinetic energy and ion fluence) of the FCVA method on the resulting thickness, structure, and mechanical properties of a-C thin films.

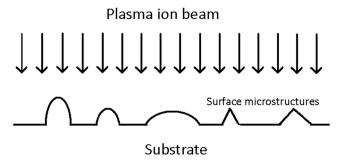
Despite significant progress in film deposition using the FCVA process, in the majority of the film deposition experiments the energetic ions impinged perpendicular to the substrate surface and, subsequently, onto the surface of the growing film. However, in applications involving film deposition on patterned surfaces, the directionality of the plasma beam may vary significantly. This is mainly the case in applications necessitating ultrathin film deposition on miniaturized structures fabricated on a substrate surface, as illustrated schematically in Fig. 1. Particularly, the mechanisms controlling thin-film synthesis by an oblique incidence plasma beam may differ from those encountered under film growth conditions of normal ion incidence, subsequently affecting the quality of the grown film. Therefore, oblique FCVA film deposition requires more in-depth examination.

The main objective of this study was to investigate the effect of the ion incidence angle on the thickness, structure, and surface roughness of a-C thin films synthesized by FCVA at different substrate bias voltages. Results from dynamic simulations, X-ray photoelectron spectroscopy (XPS), surface profilometry, and atomic force microscopy (AFM) studies are presented below to illuminate the effect of the ion incidence angle on the carbon depth profile, sputtering yield, type of hybridization, thickness, and surface roughness of FCVA-deposited nanometer-thick a-C films. The obtained results provide insight into the deposition of ultrathin a-C films under oblique ion incidence FCVA conditions and an effective approach for optimizing the ion incidence angle at various substrate bias voltages for accomplishing the growth of highly  $sp^3$  hybridized a-C films.

#### 2. Methods

#### 2.1. Deposition of carbon films

A custom-made direct-current FCVA system, described in detail elsewhere [16], was used to deposit a-C films on segments of a commercially available p-type Si(100) wafer with a root-mean-square (rms) surface roughness equal to  $\sim$ 0.2 nm. In all the FCVA experiments, the potential and current applied between the anode and the cathode were fixed at 24 V and 70 A, respectively, the C<sup>+</sup> ion flux at normal incidence (i.e., zero incidence angle) was set equal to  $\sim$ 1.5  $\times$ 



**Fig. 1.** Schematic illustration of a plasma beam interacting with a patterned solid surface. The various geometric features at the surface result in locally oblique incidence of the impinging plasma ions.

 $10^{15}$  ions/cm<sup>2</sup>·s, and the deposition time was fixed at 1 min (i.e., C<sup>+</sup> ion fluence at normal incidence equal to  $\sim 9 \times 10^{16}$  ions/cm<sup>2</sup>). The kinetic energy of the C<sup>+</sup> ions in the plasma cloud was  $\sim 20$  eV [8]. The Si substrate was affixed to the center of the sample holder, which was biased by a time-average voltage of  $\sim 25$  or  $\sim 50$  V, applied at a pulse frequency of 25 kHz. A typical waveform of the substrate pulse bias voltage is shown in Fig. 2.

Oblique plasma beam incidence is schematically depicted in Fig. 3a. The incidence angle is defined as the angle between the trajectory of the plasma beam and the normal to the substrate surface. The positively charged ions of the plasma accelerated through the electric sheath surrounding the negatively biased substrate. Accordingly, the electric

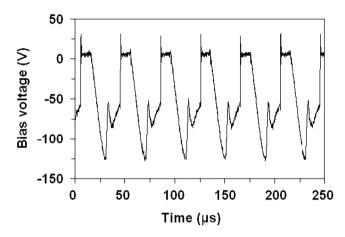
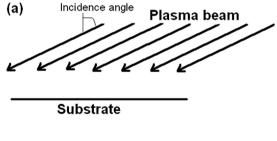


Fig. 2. Waveform of a pulse substrate bias voltage with -50~V time-average magnitude and 25 kHz frequency.



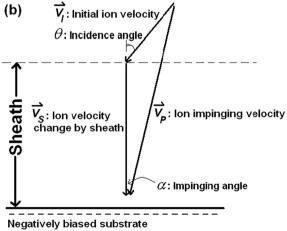


Fig. 3. (a) Plasma-surface interaction at ion incidence angle  $\theta$  and (b) schematic illustration of the change in initial ion velocity  $V_I$  and ion incidence angle  $\theta$  to ion impinging velocity  $V_P$  and ion impinging angle  $\alpha$  due to the velocity  $V_S$  introduced by the electric sheath produced at the substrate surface by the applied negative bias voltage.

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sheath increased the ion kinetic energy, while changing the magnitude and trajectory of the initial ion velocity  $V_I$ , resulting in ion impinging angle  $\alpha$  smaller than the ion incidence angle  $\theta$  and ion impinging velocity  $V_P$  greater than  $V_I$  (Fig. 3b). Because ion acceleration due to substrate pulse biasing commenced perpendicular to the substrate surface, the magnitude of the bias voltage controlled both the ion kinetic energy and the ion impinging angle.

Before the actual experiments, some preliminary depositions were performed at ion incidence angles in the range of 40– $70^{\circ}$  without rotating the substrate. The objective of these experiments was to examine whether oblique ion incidence deposition could yield anisotropic surface features, as previously observed for considerably higher ion bombarding energy [34]. For the highest substrate bias voltage applied in the present depositions (i.e., -50 V), the resulting FCVA process conditions did not produce any surface anisotropies. Nevertheless, to obtain films of uniform thickness, in all film depositions the substrate was rotated at a constant speed of 60 rpm.

A mechanical stylus profilometer (Dektak 3030 profiler, Veeco Instruments, Plainview, NY) with 0.1 nm height resolution (12.5  $\mu m$  stylus radius, 25 mg stylus force, and  $\geq \! 50 \, \mu m$  scan length) was used to measure the film thickness. This was accomplished by traversing the lightly loaded stylus tip perpendicular to the boundary of coated and uncoated (covered with a Si piece) surface regions in each sample.

#### 2.2. Simulations

Film growth was simulated with the T-DYN software (version 4.0), a dynamic simulation code based on the TRIM code [35–40], which has been verified by experimental results of atomic mixing [41], depth profiles [28,29,42,43], and sputter yield [44,45]. Details of the conditions and algorithms can be found elsewhere [41,43]. The binding energies of Si and C were set equal to 2.32 and 2.27 eV, respectively, whereas the corresponding surface binding energies were assumed to be equal to 4.7 and 7.41 eV, respectively. These binding energy values are typical of solid-state silicon and graphite.

#### 2.3. Structure and surface roughness analysis

The effects of the ion incidence angle and substrate pulse biasing on the structure (i.e., carbon atom hybridization) of the a-C films were systematically studied by XPS. This technique provides quantitative information about the bonding energy and percentages of different atomic carbon hybridizations, in conjunction with relevant information about high-energy contamination bondings [46,47]. The deposited a-C films were characterized with an XPS system (PHI 5400, Physical Electronics, Chanhassen, MN) equipped with a monochromatic X-ray source of Al-K $\alpha$  (1486.6 eV photon energy). The spectrometer was operated at a pass energy of 35.75 eV for the C1s window scan. A 0.05 eV energy step applied in increments of 50 ms was used to acquire the XPS spectra of the C1s core-level peak. The pressure in the XPS analyzing vacuum chamber was maintained below  $2.67 \times 10^{-6}$  Pa. The samples were not sputter cleaned before the XPS analysis.

The rms surface roughness of the a-C films was measured with an AFM setup (Dimension 3100, Veeco Instruments, Plainview, NY), using a  $1\times1~\mu\text{m}^2$  scan area. The AFM was operated in tapping mode at 259.332 kHz drive frequency and 2 Hz scan rate.

#### 3. Results and discussion

A model of the ion incidence onto the substrate surface was developed for the T-DYN simulations. The ion fluence on the substrate surface was calculated by multiplying the ion fluence normal to the surface (i.e.,  $\sim 9 \times 10^{16}$  ions/cm²) by the cosine of the ion incidence angle (Fig. 3b). The electric sheath due to substrate pulse biasing changed the velocity of the impinging ions, consequently changing the kinetic energy of the bombarding C<sup>+</sup> ions. The change in ion kinetic energy was controlled by

the substrate bias voltage, not by the ion incidence angle. For example, for a -50 V time-average bias voltage and -20 eV initial ion kinetic energy, the kinetic energy of the C<sup>+</sup> ions impinging onto the substrate surface was equal to -70 eV, regardless of the ion incidence angle. However, the ion impinging angle was affected by both the ion incidence angle and the magnitude of the substrate bias voltage. The direct and indirect process parameters, including the change in ion velocity  $V_S$  and the impinging angle (Fig. 3b), are related through the following relations:

$$E_P = E_I + E_S$$

$$E_I = \frac{1}{2}m_C V_I^2$$

$$E_P = \frac{1}{2}m_C V_P^2$$

$$V_P^2 = (V_I \sin\theta)^2 + (V_I \cos\theta + V_S)^2$$

$$\Phi_P = \Phi_I \cos\theta$$

where  $E_P$  is the kinetic energy of the ions impinging onto the substrate surface,  $E_I$  is the initial ion kinetic energy ( $\sim$ 20 eV),  $E_S$  is the change in ion kinetic energy caused by the electric sheath (substrate bias voltage),  $m_C$  is the mass of a carbon ion (1.994  $\times$  10<sup>-23</sup> g), and  $\Phi_I$  and  $\Phi_P$  are the initial ion incidence fluence and the ion fluence on the substrate surface, respectively. Calculated values of  $V_S$  and  $\alpha$  for -25 and -50 V substrate bias voltages are given in Table 1. These data were input in the T-DYN simulations of the carbon depth profiles.

Fig. 4 shows carbon depth profiles in a Si substrate simulated with the T-DYN code for ion incidence angles in the range of 0–80°. In all simulation cases, the  $\alpha$ -C film thickness decreased with the increase of the ion incidence angle due to the decrease of the ion fluence (Table 1). Moreover, the increase of the substrate bias voltage enhanced Si-C intermixing. This is evinced by comparing the depth range with atomic carbon <100 %, for a given ion incidence angle. The enhancement of Si-C intermixing was attributed to the intensified direct and recoil implantation caused by the increase of the ion kinetic energy. Thus, the film thickness strongly depended on the substrate bias voltage (ion kinetic energy) and the ion incidence angle.

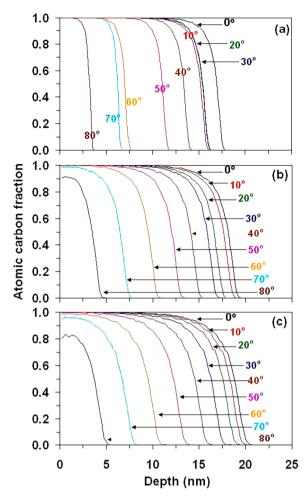
A comparison of the a-C film thickness values obtained from the T-DYN simulations (Fig. 4) with experimentally measured values (Fig. 5) showed a fair agreement, except for some small deviations, which were most likely due to plasma intensity fluctuations during film deposition. The slight increase of the film thickness in the ion incidence angle range of 0– $20^{\circ}$  under energetic C<sup>+</sup> ion bombardment (Fig. 5b and c) was attributed to the dominant effect of ion implantation at small incidence

**Table 1** Ion velocity change  $V_S$  due to the electric sheath at the substrate surface generated by the applied bias voltage, ion impinging angle  $\alpha$ , and ion fluence at the substrate surface  $\Phi_P$  versus ion incidence angle  $\theta$ .

$\theta$ (deg.)	Substrate bias voltage (V)				$\Phi_P  ( imes 10^{16}  \mathrm{ions/cm^2})$
	-25		-50		
	$V_S$ (m/s)	$\alpha$ (deg.)	$V_S$ (m/s)	$\alpha$ (deg.)	
0	8935	0.0	15,562	0.0	9.00
10	9026	6.6	15,689	5.3	8.86
20	9307	13.2	16,076	10.5	8.46
30	9796	19.5	16,740	15.5	7.79
40	10,530	25.4	17,708	20.1	6.89
50	11,559	30.7	19,014	24.2	5.79
60	12,951	35.3	20,700	27.6	4.50
70	14,782	38.8	22,797	30.2	3.08
80	17,116	41.0	25,322	31.8	1.56

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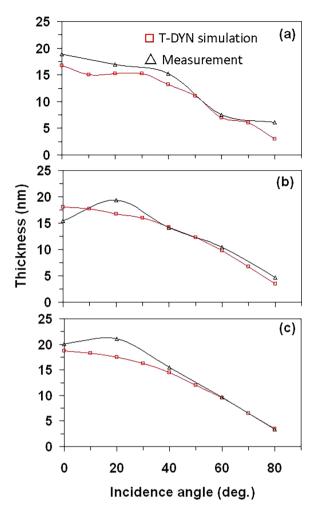
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**Fig. 4.** Carbon depth profiles simulated with the T-DYN code for Si substrate,  $C^+$  ion impinging angle in the range of  $0{-}80^\circ$ , and time-average substrate bias voltage equal to (a) 0 V, (b)  ${-}25$  V, and (c)  ${-}50$  V. The  $C^+$  ion fluence in the plasma cloud was set equal to  $9\times10^{16}~ions/cm^2$ , corresponding to 1 min film deposition in the FCVA experiments. The  $C^+$  ion fluence at the Si surface was calculated by multiplying the ion fluence in the plasma by the cosine of the incidence angle, defined in Fig. 3. The  $C^+$  ion fluence corresponding to each ion impinging angle is given in Table 1.

angles, whereas the decreasing trend of the film thickness in the ion incidence angle range of  $20\text{--}80^\circ$  was ascribed to the decrease of the ion fluence (Table 1,  $\Phi_P = \Phi_I \cos\theta$ ) and the enhancement of ion sputter etching at high ion incidence angles. The results shown in Figs. 4 and 5 illuminate the profound effect of the ion incidence angle on the thicknesses of the intermixing layer and the *a*-C film. Additionally, since the deposition time in all FCVA experiments was fixed at 1 min, the film thickness data (Fig. 5) also represent deposition rates at different ion incident angles and substrate bias voltages.

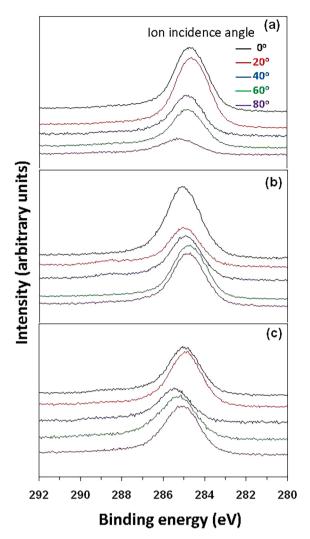
Fig. 6 shows XPS C1s core-level peaks of a-C films synthesized under deposition conditions of varying ion incidence angle and substrate bias voltage. For zero substrate bias voltage, the position of the C1s peak gradually shifted to a higher binding energy with the increase of the ion incidence angle from 0 to 80° (Fig. 6a). However, for a substrate bias voltage equal to -25 V, a gradual shift of the C1s peak to a lower binding energy occurred with increasing ion incidence angle (Fig. 6b), whereas the further increase of the substrate bias voltage to -50 V did not yield a clear trend (Fig. 6c). Interestingly, for -50 V bias voltage, the C1s peak with the highest binding energy corresponded to an ion incidence angle equal to  $40^\circ$ . Considering the dependence of the binding energy of the C1s peak on the oxidation state and local chemical environment, affected by the adsorption of oxygen from the atmo-sphere and the



**Fig. 5.** T-DYN simulation results and profilometry measurements of a-C film thickness versus ion incidence angle for time-average substrate bias voltage equal to (a) 0 V, (b) –25 V, and (c) –50 V.

carbon surface reactivity influenced by the intensity of energetic ion bombardment (substrate pulse biasing effect), the observed peak shifts may be associated with changes in the surface chemistry of the a-C films upon exposure to the ambient.

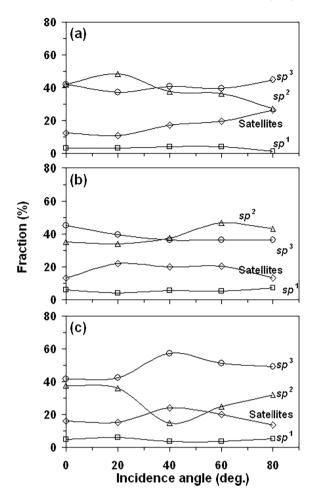
After performing a Shirley inelastic background subtraction [48], the XPS C1s core-level peaks were deconvoluted to extract information about the atomic carbon hybridization in each film. Details about the deconvolution methodology can be found elsewhere [46,47,49]. The carbon species in the a-C films exhibited  $sp^1$ ,  $sp^2$ , and  $sp^3$  hybridizations, with some high-energy surface species (referred to as the satellite peaks) attributed to physical adsorption of airborne contaminants also present in the spectra. Fig. 7 shows the fraction of each carbon component as a function of ion incidence angle and substrate bias voltage. The fraction of  $sp^1$  hybridization was very small and constant in all a-C films. However, both the  $sp^2$  and  $sp^3$  hybridizations exhibited different trends and notable fluctuations. Specifically, while the  $sp^2$  and  $sp^3$  fractions varied between  $\sim 30$  % and  $\sim 50$  % for zero and  $\sim 25$  V substrate bias voltage, showing indistinguishable dependence on ion incidence angle, for -50 V substrate bias voltage, they demonstrated significantly different variations. In fact, a-C films with the highest  $sp^3$  (~58 %) and lowest  $sp^2$  (~14 %) contents were obtained for a  $40^{\circ}$  ion incidence angle. According to the subplantation model [28–30], the energetic C<sup>+</sup> ions penetrated up to a depth depending on the ion kinetic energy, resulting in carbon-induced densification and the development of a compressive mechanical environment, which was conducive to  $sp^3$  hybridization. Accordingly, the enhancement of  $sp^3$  hybridization was controlled by the intensity of H. Zhang and K. Komvopoulos Thin Solid Films 784 (2023) 140045



**Fig. 6.** XPS spectra of the C1s core-level peak of a-C films for ion incidence angle between  $0^\circ$  (normal incidence) and  $80^\circ$  and time-average substrate bias voltage equal to (a) 0 V, (b) –25 V, and (c) –50 V.

carbon-carbon collisions, which depended on the carbon concentration [50]. Consequently, because the increase of the ion incidence angle led to the decrease of the implantation depth of the impinging  $C^+$  ions, carbon-carbon collision cascades were mostly confined within the near-surface region, contributing to the densification enhancement and the evolution of compressive stresses that favored  $sp^3$  hybridization. However, above a critical ion incidence angle (i.e.,  $40^\circ$ ), a slight decrease of the  $sp^3$  fraction was encountered due to the breakage of some of the  $sp^3$  carbon bonds as a result of more intense ion bombardment, resulting in  $sp^3$ -to- $sp^2$  re-hybridization (Fig. 7c). Thus, the existence of a critical ion incidence angle for maximum  $sp^3$  hybridization (i.e.,  $40^\circ$  critical ion incidence angle for -50 V substrate bias voltage) could be attributed to lessening of the carbon-carbon collisions (decrease in carbon concentration) with the increase of the ion incidence angle.

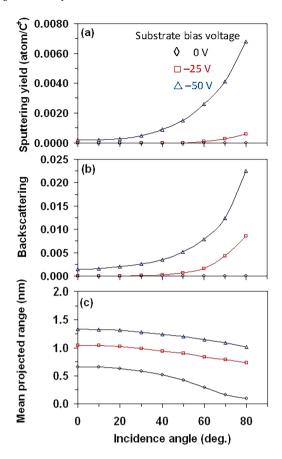
Whereas the application of a negative substrate bias voltage intensified the ion bombardment, it also produced an ion impingement angle a smaller than the ion incidence angle  $\theta$  (Table 1). This explains the slightly higher  $sp^3$  fraction for ion incidence angles less than  $\sim 20^\circ$  (Fig. 7b and c), for which the ion impinging angle was small (i.e., nearly normal ion incidence). Earlier studies showed a dependence of the  $sp^3$  fraction of carbon films on substrate bias voltage for normal ion incidence [16,20,21]. The  $sp^3$  fraction of carbon films having energetic C<sup>+</sup> ions as film precursors has been reported to increase with the magnitude of the substrate bias voltage up to about -100 V, corresponding to  $\sim 120$ 



**Fig. 7.** Fractions of different atomic carbon hybridizations calculated from the deconvoluted C1s core-level peak of a-C films versus ion incidence angle for time-average substrate bias voltage equal to (a) 0 V, (b) -25 V, and (c) -50 V.

eV C<sup>+</sup> ion kinetic energy, and subsequently decrease with the increase of the bias voltage beyond -100 V [1,5,8,20,51]. Because the -25 V substrate bias voltage increased the kinetic energy of the bombarding C<sup>+</sup> ions only to  $\sim$ 45 eV, the  $sp^3$  fraction did not change significantly with the ion incidence angle (Fig. 7b). However, increasing the substrate bias voltage to -50 V (i.e., ~70 eV ion kinetic energy) changed significantly the dependence of the  $sp^2$  and  $sp^3$  fractions on the ion incidence angle (Fig. 7c). Notably, the highest  $sp^3$  fraction corresponding to  $40^\circ$  ion incidence angle was found to be higher than that reported for higher (-100 V) substrate bias voltage, but zero ion incidence angle [16,43]. This difference in  $sp^3$  fraction may be related to the development of a more compressive mechanical environment due to the increased carbon concentration at the surface under oblique ion incidence, which intensified carbon-carbon collision cascades that favored sp<sup>3</sup> hybridization. Even though the sp<sup>3</sup> fraction decreased slightly in the depositions with ion incidence angles greater than 40° and -50 V substrate bias voltage, it remained much higher than the  $sp^2$  fraction. Whereas the predominance of sp<sup>3</sup> hybridization may also be attributed to preferential sputtering of the  $sp^2$  hybridized carbon domains, this conjecture was not supported by the analysis of the T-DYN simulation results, which showed negligible sputtering yield (Fig. 8a) and backscattering (Fig. 8b) under the present deposition conditions. A more likely supposition is that oblique incidence of the energetic C<sup>+</sup> ions activated atomic collisions at the growing film surface, transferring energy that increased the momentum of surface atoms, consecutively enhancing sp<sup>3</sup> hybridization, as opposed to perpendicularly impinging ions that were implanted deeper into the substrate. Indeed, results of the mean projected range (Fig. 8c) showed a

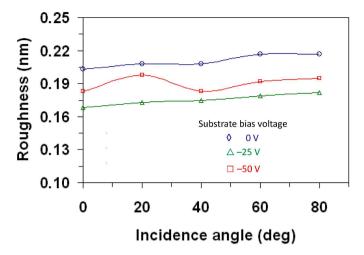
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**Fig. 8.** T-DYN simulation results of (a) sputtering yield, (b) backscattering, and (c) mean projected range for C<sup>+</sup> ions impinging onto a Si surface versus ion incidence angle and time-average substrate bias voltage equal to 0, –25, and –50 V.

decrease in ion travel distance with increasing ion incidence angle, suggesting that carbon-carbon atom collisions and film densification were confined at the outermost surface region of the film. Thus, the decrease of the ion fluence with the increase of the ion incidence angle (Table 1) was compensated by the confinement of carbon atom collisions within the near-surface region of the growing film, which promoted  $sp^3$  hybridization. Consequently, the high  $sp^3$  content can be ascribed to the enhancement of surface atom collision cascades, with optimum conditions encountered under FCVA conditions of  $40^\circ$  ion incidence angle and -50 V substrate bias voltage.

In addition to the ion incidence angle effect on the thickness and structure of the FCVA-deposited a-C films, the resulting surface roughness is also of high importance in applications requiring ultrasmooth surfaces, such as microelectronics, photonics, and magnetic recording technologies. Fig. 9 shows the dependence of the a-C film roughness on the ion incidence angle for various substrate bias voltages. The slight surface roughening caused by the increase of the ion incidence angle observed in all depositions can be associated with the intensification of resputtering under oblique ion bombardment. This conjecture is supported by the decrease of the film thickness with increasing ion incidence angle (Fig. 5). The somewhat smoother films synthesized under a substrate bias voltage of -25 V may be related to less atomic displacement in these films compared to the films deposited under a substrate bias voltage of -50 V. Comparatively less sp<sup>3</sup> hybridization and higher surface roughness was observed in previous studies [30,46]. This suggests that the smoother a-C films synthesized under conditions of  $40^{\circ}$  ion incidence angle and -50 V substrate bias voltage may be correlated with the high sp<sup>3</sup> fraction of these films (Fig. 7c), attributed to the



**Fig. 9.** Variation of rms surface roughness of a-C films with ion incidence angle for time-average substrate bias voltage equal to 0, -25, and -50 V.

compressive mechanical environment at the growing film surface produced under oblique ion incidence deposition conditions.

#### 4. Conclusions

The thickness, structure, and roughness of nanometer-thick a-C films deposited by the FCVA technique for ion incidence angles in the range of  $0-80^{\circ}$  and time-average substrate pulse bias voltage of magnitude equal to 0, -25, and -50 V were characterized in the light of T-DYN simulation results and XPS, surface profilometry, and AFM measurements. Carbon film growth,  $\mathit{sp}^3$  hybridization, and surface texturing at oblique ion incidence were interpreted in the context of simulation and experimental results. The C<sup>+</sup> ion fluence on the substrate surface decreased with the increase of the ion incidence angle, consequently leading to deposition of thinner films. Carbon atom hybridization was also affected by the ion incidence angle and applied substrate bias voltage. a-C films with the highest  $sp^3$  fraction (~58 %) were deposited under FCVA plasma conditions of 40° ion incidence angle and -50 V substrate bias voltage. The increase of the sp<sup>3</sup> hybridization was attributed to carbon-carbon atomic collisions at the growing film surface and the densification induced by direct and recoil implantation processes controlled by the ion incidence angle and substrate bias voltage. The marginal increase of the surface roughness of the a-C films with the ion incidence angle was correlated with the enhancement of sputter etching under oblique ion incidence. The simulation-experimental approach presented in this study provides a ground base for further investigations aimed to optimize the ion incidence angle for depositing smooth, highly sp3 hybridized carbon thin films under various substrate bias voltages.

#### CRediT authorship contribution statement

**Hanshen Zhang:** Conceptualization, Writing – original draft. **Kyriakos Komvopoulos:** Supervision, Writing – review & editing, Resources.

#### **Declaration of Competing Interest**

The authors declare no competing interests.

#### Data availability

Data will be made available on request.

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