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EFFECT OF ENERGETIC ION BOMBARDMENT DURING THE GROWTH OF HYDROGENATED AMORPHOUS CARBON THIN FILMS

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ABSTRACT

Hydrogenated amorphous carbon (a-C:H) thin film growth using plasma-assisted deposition is studied using Monte Carlo based simulation. The effect of energetic bombardment of the ionized depositing species as well as ionized buffer gas species on the film growth and the resulting film properties is investigated. The ion energies that assist the a-C:H film growth from low density structures to high density structures such as diamond-like carbon (DLC) are used and the effect of energy and composition of the depositing species on the C-C and C-H bonding and the film structure are analyzed. It is found that the ion bombardment favors the formation of a-C:H films with low H contents, high density and superior mechanical strength of the resulting thin films and is therefore an effective way to tailor-made a-C:H thin film growth for specific applications.

Indexing terms/Keywords

hydrogenated amorphous carbon; magnetron sputtering; diamond-like carbon; plasma discharges; hydrocarbon precursor.

Academic Discipline And Sub-Disciplines

Science; Physics

SUBJECT CLASSIFICATION

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TYPE (METHOD/APPROACH)

Monte Carlo based simulation and modeling

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INTRODUCTION

Amorphous carbon (a-C) thin films exhibit adjustable mechanical, optical and electrical properties finding their applications ranging from hard coatings to biomedical applications [1 – 3]. The properties of a-C thin films are controlled by controlling how the C atoms bond to each other (i.e. their hybridization states namely sp^1, sp^2 and sp^3 bond configurations) and with other elements such as H, N etc [4]. Depending on the bonding configuration (mainly sp^3/sp^2 bond ratio) a-C can be synthesized in various forms. These include low density structures such as graphite-like carbon (GLC), high density structures such as diamond-like carbon (DLC) and ultra-high density structures such as tetrahedral a-C (ta-C) [4,5]. The incorporation of other elements gives rise to the modified forms of these structures such as hydrogenated a-C (a-C:H) and CN_x thin films that are formed by incorporating H and N into the films respectively. These modified film structures allow for achieving additional functionalities from these thin films [4].

Commonly a-C:H thin films are synthesized using a hydrocarbon precursor gas such as CH_4, C_2H_2 etc. in a chemical vapor deposition (CVD) based process or a physical vapor deposition (PVD) based process [6]. The type of a-C:H and hence the resulting film properties depend on the composition, amount and energy of the depositing species. For plasma-assisted PVD based methods such as magnetron sputtering the sp^3/sp^2 bond ratio is mainly controlled by the energy and flux of the ionized depositing species [4]. The energetic bombardment of ionized depositing species during the a-C:H film growth brings about several changes in the structure and understanding the plasma-film surface interactions for these thin films is essential for tailoring the film properties that are relevant for particular application [7].

In this work, we study a-C:H film growth for a plasma-assisted deposition process. We investigate the influence of energetic bombardment of ionized depositing species on the growth, structure as well as on the resulting film properties using Monte Carlo based computer simulations. We analyze plasma-film surface interactions using inert and hydrocarbon ionized gas species as well as sputtered C and establish a correlation between the plasma chemistry, plasma energetics and film properties.

FILM GROWTH AND SIMULATION

In plasma-assisted deposition process, such as magnetron sputtering where a-C:H films are sputtered deposited in an Argon+hydrocarbon gas ambient (such as C_2H_2), the film growth is affected by the plasma composition, plasma-chemical interactions as well as plasma-film surface interactions [6]. The hydrocarbon precursor gas undergoes dissociation and ionization through electron-impact interactions in the plasma discharge giving various reaction products along with H and C [8,9]. The film forming flux therefore typically constitutes hydrocarbon radicals and ionized species, atomic and molecular H as well as sputtered C. The ionized deposition species which possess an energy higher than the surface penetration threshold, which is typically 32 eV for a carbon surface, are implanted into subsurface region during the film growth where they bring about structural changes such as increase in the local density of C atoms or removal of H atoms thereby reducing C-H bonds [4,8]. The surface penetration threshold, E_p, is expressed as [4]:

$$E_p \sim E_d - E_B \tag{1}$$

Where E_d is the displacement energy and E_B is the surface binding energy.

The structural changes such as densification, is described in the form of so-called subplantation model for amorphous carbon which is given as [4]:

$$\frac{\Delta\rho}{\rho} = \frac{f\emptyset}{1 - f\emptyset + 0.016\,(\frac{E_i}{E_o})^{5/3}} \tag{2}$$

Here $\frac{\Delta\rho}{\rho}$ represents the change in the film density ρ in response to the implantation of fraction f of the total ion flux $\emptyset$ with an incident energy E_i and activation energy of E_o.

Typically, the dense amorphous carbon films are synthesized with an energy of about 100 eV per deposited C atom [4]. For the case of a-C:H using a hydrocarbon precursor, the radicals and ionized hydrocarbon species that contain two or more carbon atoms, such as C_2H radical or $C_2H_2^+$ ion, split upon reaching the growing film surface [9] and the incident energy E_i is shared among the constituents. The energy per deposited C atom E_c in this case is given as [10]:

$$E_c = \frac{m_c E_i}{2m_c + 2m_H} \tag{3}$$

Where m_C and m_H are respectively the masses of C and H atoms.

In order to investigate the role of energetic bombardment of ionized species in a plasma-assisted growth of a-C:H thin films, we considered the films with a thickness of 500 nm. One of the most important factor that determines the properties of a-C:H thin films is H content. Typically a-C:H films contain 20% – 50% atomic H with varied mass densities [10,11]. We employ a-C:H thin films with a H content of 20 at.% and a mass density of 1.8 g/cm^3. Plasma species consisting of sputtering gas species, Ar^{1+}, the atomic hydrogen, H^{1+} and the sputtered carbon, C^{1+} which are also the major film forming species are considered. In a typical sputtering based deposition of a-C:H without any substrate bias potential, the ions

reach to the substrate with an energy corresponding to the floating potential which is typically about 5 – 10 eV [12]. Whereas the most prominent structural changes in a-C thin films are caused by C^{1+} ions with an energy of ~ 100 eV at which the ions are implanted to subsurface regions giving rise to denser a-C structures such as DLC and ta-C as shown in Eq. 2 [4]. We therefore considered energies of 10 eV, 100 eV and 200 eV for bombarding ions. All the simulations are performed using SRIM [13]

RESULTS AND DISCUSSION

Fig.1 shows the penetration depths of Ar^{1+}, C^{1+} and H^{1+} ions of different energies into an a-C:H thin film. For all of the ions, it is observed that the ions undergo a shallow implantation into subsurface region limiting their penetration to about 10 nm at an incident energy of 10 eV. The ion penetration is found to increase with an increased energy of the ions. For Ar^{1+} ions (see Fig. 1a), the most of the ions (represented by the peak count rate) reach to about 20 nm whereas the tail of the ion penetration depth extends to about 40 nm for 200 eV. This could be considered a low penetration with regards to the thickness of the film (500 nm) and could be a consequence of larger mass (and size) of Ar^{1+} ion as compared to the film constituents i.e. C and H. Another important factor for ion penetration is the surface penetration threshold energy which is about 32 eV for a carbon film surface. This means that 10 eV Ar^{1+} ion does not have sufficient energy to penetrate deeper into the surface of the thin film. At energies higher than the surface penetration threshold, for example 100 eV, the ions are likely to overcome the energy barrier and reach to subsurface regions. However, the energy transfer between an incident ion and the atoms in the growing film limits the penetration of the incident ions and mostly the effect of energetic ion bombardment is limited to structural changes in the near surface region of the film. This is evident from Fig. 2a where a 100 eV Ar^{1+} ion is found to lose about 6 eV of its energy to carbon atoms per Å of the film thickness. On the other hand, the energy transfer from incident Ar1+ ions to much lighter H atoms in the film is very small.

A similar behavior for C^{1+} ions (Fig. 1b) is observed as that for Ar^{1+} ions. Although the C atoms are much smaller in size as compared to Ar but their penetrations are not higher than Ar. This could be due to the fact that the incident C^{1+} ions impart higher amount of energies to C and H atoms in the film causing substantial amount of energy loss which leads to low penetration depths. This can be seen from Fig. 2a where a 100 eV C^{1+} ion loses most of its energy to C atoms (due to equal masses) of the film. The energy transfer from C^{1+} ions to H atoms in the film is also substantial (see Fig. 2b) The ion penetration distributions for H^{1+} ions (Fig. 1c) are substantially different as compared to Ar^{1+} and C^{1+}. The distributions are found to be broader and H^{1+} ions penetrate further into subsurface regions of an a-C:H film where they reach as deep as about 60 nm for an incident energy of 200 eV. The tails of the distributions for H^{1+} extend to much larger depth (about 100 nm) at this energy. The larger penetrations of H^{1+} ions is due to their smaller size as well as low amount of energy that they lose to C atoms (that constitute 80% of the film) into the film. This is seen in Fig. 2a where it is found that a 100 eV H^{1+} ions incident on an a-C:H film during the growth imparts almost negligible energy to C atoms but a substantial energy transfer occurs to the H atoms in the film (see Fig. 2b).

The energy transfer from an incident ion to the film constituting atoms usually results in the displacement of the latter [14]. This leads to the formation of vacancy-interstitial pair. Fig. 3 shows the number of C and H vacancies in a-C:H film as a result of ion bombardment during the film growth [14]. It is found that the number of C and H vacancies increases with an increase of the energy of the incident ion. For C atoms (Fig. 3a), the number of vacancies formed due to Ar^{1+} and C^{1+} ions at all energies is almost similar whereas incident H^{1+} ions do not contribute substantially to C vacancy formation. In an a-C:H film, typically C atoms have a displacement energy of 25 eV [4] and since the incident H^{1+} ions do not impart significant energies to C atoms (as seen in Fig. 2a), therefore the C atom vacancy formation from H^{1+} ions is unlikely. The H vacancy formation (see Fig. 3a) due to C^{1+} and H^{1+} ions is comparable while a lower number of vacancies are formed due to incident Ar^{1+} ions. Since penetration of Ar^{1+} ions is shallow (Fig. 1a) and they also do not contribute adequately to H vacancy formation, therefore the H in the a-C:H films is not largely affected by Ar^{1+} ion bombardment. This implies that the Ar^{1+} ions will mostly affect the H that is chemisorbed to the film surface. The larger H vacancies formed due to C^{1+} and H^{1+} ions as well as higher penetration of H^{1+} ions into the film means that the H content in the film is mainly controlled by C^{1+} and H^{1+} ion bombardment. The H displacement energy is lower (2.5 eV) [15] as compared to C (25 eV) which implies that H atoms bonded to C atoms in an a-C:H film are readily displaced by both C^{1+} and H^{1+} ions. The displaced H atoms either rearrange themselves to form C-H bonds with C atoms or they are combined with other displaced H atoms to form H_2 molecules which diffuse to the film surface and desorb into the gas phase [16]. The overall effect of the ion bombardment is therefore a reduced amount of H into the film. Since the H atoms enter into C-H sp^3 bonds which are weaker than C-C sp^2 or C-C sp^3 bonds [17], therefore the reduction of H through ion bombardment results in less number of C-H bonds and higher number of C-C bonds. This gives rise to denser thin films which also exhibit higher mechanical hardness.

During the a-C:H film growth, the ion bombardment also influences the film surface structure. From the gas phase, the atomic H chemisorbs on the surface. The depositing C atoms can thus bond to other C atoms or with H. The ion bombardment however, can remove the bonded C and H atoms by breaking the C-H bonds. This can be seen from partial sputtering yields of C and H presented in Table I for different incident ions having different energies. The partial sputtering yields of C and H increase with an increase in the energy of the ions. For 10 eV ions, the partial sputtering yields of both C and H are negligible. The highest sputtering yields for C are obtained by C^{1+} ion bombardment and for H by H^{1+} ion bombardment. These results agree well with the penetrations of the incident ions presented in Fig. 1 where Ar^{1+} ions were found to exhibit low penetration and therefore affecting mainly the surface of the growing film whereas C^{1+} and H^{1+} ions penetrate deeper into subsurface regions and therefore affecting the film properties by the ion implantation.

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CONCLUSIONS

The effect of energetic ion bombardment was investigated for the growth of a-C:H thin films. It was found that the structure and hence the resulting film properties can be tailored by the energetic ion bombardment. The energetic ion bombardment was found to affect the surface structure, C-C and C-H bond formation which consequently affects the film properties.

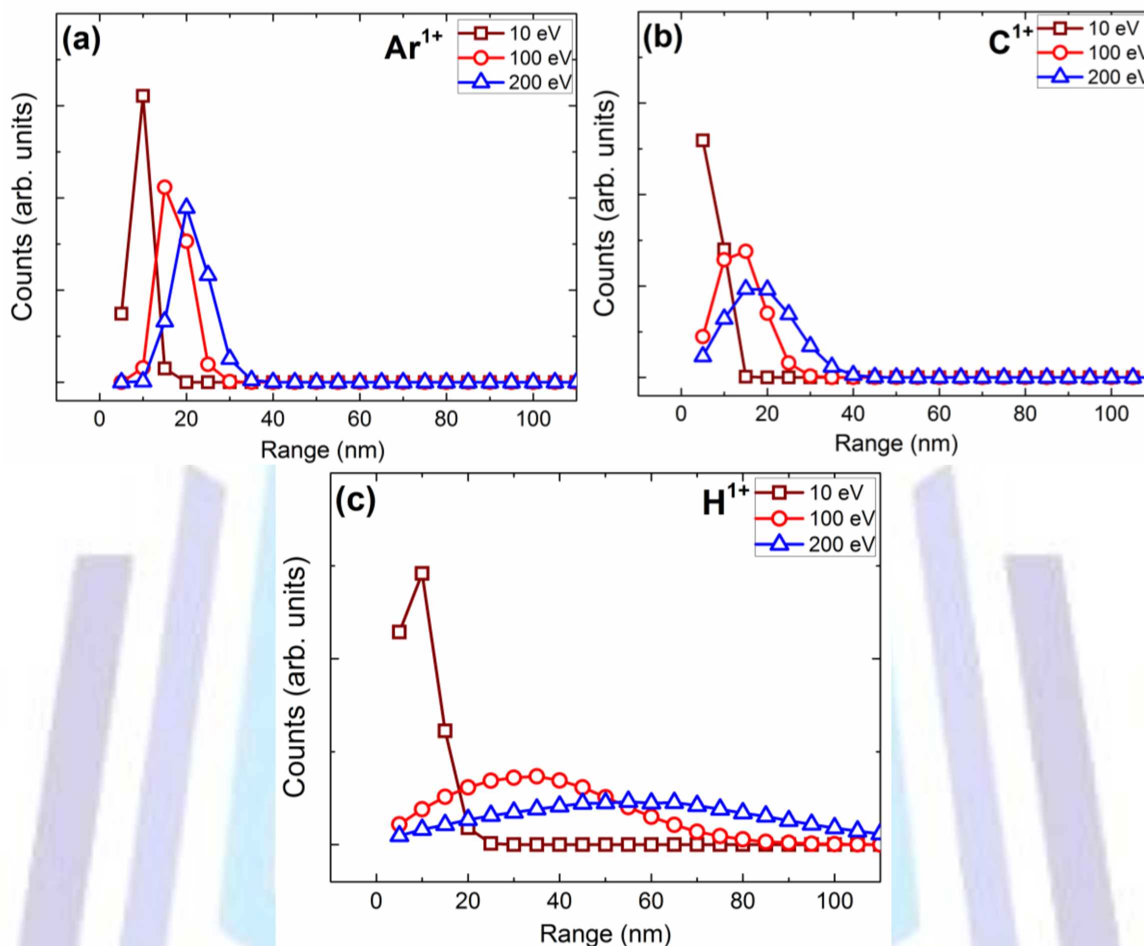

Fig. 1: The penetration depths of (a) Ar^{1+}, (b) C^{1+} and (c) H^{1+} ions of different energies into a 500 nm thick a-C:H thin film with mass density of 1.8 g/cm^3 and H content of 20%. For clarity, the ion ranges are shown up to only 100 nm.

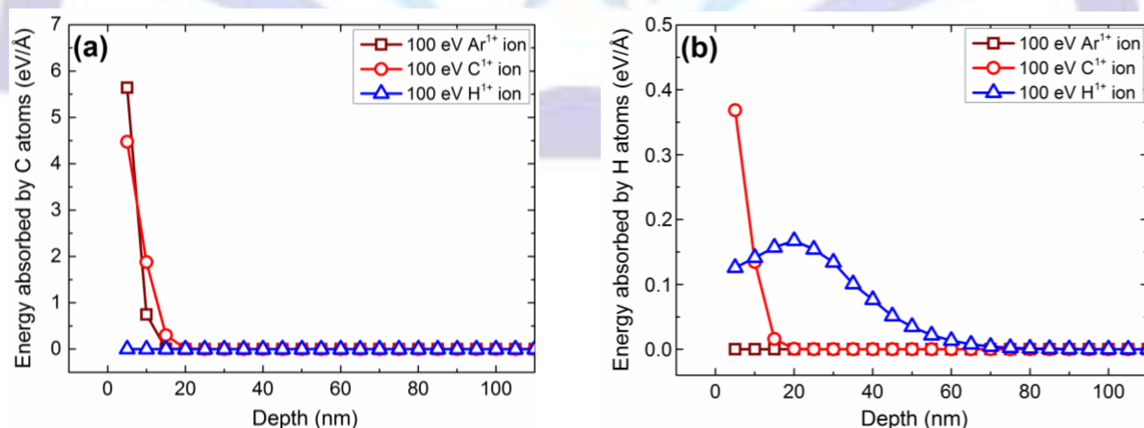

Fig. 2: Energy absorbed (Recoil energy) by (a) C and (b) H atoms of a-C:H thin film under the ion bombardment of Ar^{1+}, C^{1+} and H^{1+} ions with each having an incident energy of 100 eV.

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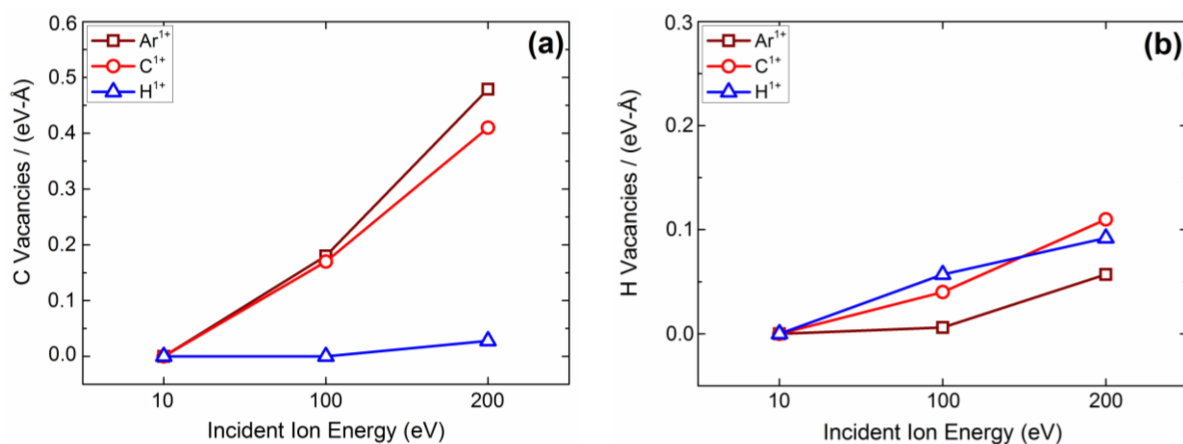

Fig. 3: (a) C and (b) H vacancies created by the bombardment of Ar^{1+}, C^{1+} and H^{1+} ions of different incident energies during the growth of a-C:H thin film.

Table 1: Partial sputtering yields of C and H of a-C:H thin films for Ar^{1+}, C^{1+} and H^{1+} ions of different energies.

Incident Ion	Energy (eV)	C sputtering yield (atoms/ion)	H sputtering yield (atoms/ion)
Ar^{1+}	10 100 200	0 0.002 0.016	0 0.001 0.011
C^{1+}	10 100 200	0 0.042 0.085	0 0.023 0.047
H^{1+}	10 100 200	0 0 0.006	0 0.007 0.008

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