# A strategy for increased carbon ionization in magnetron sputtering discharges

Asim Aijaz, Kostas Sarakinos, Daniel Lundin, Nils Brenning and Ulf Helmersson



Original Publication:

Asim Aijaz, Kostas Sarakinos, Daniel Lundin, Nils Brenning and Ulf Helmersson, A strategy for increased carbon ionization in magnetron sputtering discharges, 2012, Diamond and related materials, (23), 1-4.
http://dx.doi.org/10.1016/j.diamond.2011.12.043

# A strategy for increased carbon ionization in magnetron sputtering discharges

Asim Aijaz,*[1] Kostas Sarakinos,[1] Daniel Lundin,[1] Nils Brenning,[1,2] Ulf Helmersson[1]

[1]Plasma and Coatings Physics Division, IFM-Materials Physics, Linköping University, SE-58183, Linköping Sweden

[2]Division of Space and Plasma Physics, School of Electrical Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

* Corresponding Author. E-mail: asim@ifm.liu.se

| | |
|---|---|
| Complete Address: | Asim Aijaz<br>Plasma and Coatings Physics Division,<br>IFM-Materials Physics, Linköping University,<br>SE-58183 Linköping, Sweden |
| Phone: | 0046-13-286616 |
| Fax: | 0046-13-137568 |


**Abstract**

A strategy that facilitates a substantial increase of carbon ionization in magnetron sputtering discharges is presented in this work. The strategy is based on increasing the electron temperature in a high power impulse magnetron sputtering discharge by using Ne as the sputtering gas. This allows for the generation of an energetic $C^+$ ion population and a substantial increase in the $C^+$ ion flux as compared to a conventional Ar-HiPIMS process. A direct consequence of the ionization enhancement is demonstrated by an increase in the mass density of the grown films up to 2.8 g/cm$^3$; the density values achieved are substantially higher than those obtained from conventional magnetron sputtering methods.


**Keywords:** HiPIMS; HPPMS; Carbon ionization; tetrahedral amorphous carbon; Diamond-like carbon

## 1. Introduction

In film growth processes that develop via condensation from the gas phase such as physical vapour deposition (PVD) — large fractions of ions among the film forming species have been shown to beneficially influence the synthesis of tailor-made films [1-3]. In plasma-assisted PVD processes, target (source) material ions are typically generated by collisions either with energetic electrons (referred to as electron impact ionization) or with metastable buffer gas (typically Ar) atoms (referred to as Penning ionization) [4]. The generation of highly ionized fluxes requires that the electron impact mechanism is promoted [5]. The probability of such an impact can be described by using the ionization mean free path $\lambda_{miz}$, which is determined by the velocity of the sputtered neutrals $v_s$, the plasma density $n_e$, and the ionization rate co-efficient $k_{miz}$, through the expression [5],

$$\lambda_{miz} = v_s / \left( k_{miz} n_e \right) . \qquad (1)$$

It is evident from Eq. (1) that one way to decrease $\lambda_{miz}$ and, thereby, promote electron impact ionization is to increase the plasma (electron) density. In magnetron sputtering based PVD, this route has been successfully implemented for most common metals such as Cu, Ti, Ta, and Al which exhibit ionization energies ($E_i$) between 6 and 8 eV using high power impulse magnetron sputtering (HiPIMS), which generates discharges with relatively high plasma densities (in the order of $10^{18}$-$10^{19}$ $m^{-3}$) [4,6]. However, this route is challenged when non-metals such as carbon, which exhibits a significantly higher $E_i$ value of 11.26 eV, is considered. For instance, Sarakinos et al. have shown that the dominant ionized species in a HiPIMS discharge are $Ar^+$ ions while $C^+$ ions constitute only ~1% of the total ionic contribution [7]. Moreover, DeKoven *et al.* have shown that in HiPIMS discharges the $C^+/C$ ratio does not exceed 5% [8]. This is a direct consequence of the large $E_i$ and small electron impact ionization cross-section of carbon; it also implies that a significant part of the electrons do not possess sufficient energy to ionize the sputtered carbon. Ionization degrees that approach 100% are essential for the synthesis of technologically relevant forms of carbon, e.g., tetrahedral amorphous carbon (ta-C) [9-12]. Currently, this can be achieved by plasma based PVD techniques that provide much higher electron densities (in the order of $10^{21}$ $m^{-3}$), e.g., filtered cathodic vacuum arc (FCVA) and pulsed laser deposition (PLD) [13-15]. Increasing the degree of ionization of carbon in plasma with electron densities approaching $10^{19}$ $m^{-3}$ would facilitate the widespread implementation of magnetron sputtering based techniques for the synthesis of ta-C. This is of great technological relevance owing to inherent advantages of magnetron sputtering such as conceptual simplicity, scalability, cost efficiency and film uniformity.

An alternative strategy for promoting electron impact ionization is via the rate coefficient $k_{miz}$ in Eq. (1). This coefficient is defined by the expression [5],

$$k_{miz}(T_e) = k_0 \exp\left(-E_0/T_e\right), \tag{2}$$

where $k_0$ and $E_0$ are material dependent constants which can be extracted from experiments or computer simulations [5,16,17]. It is evident from Eq. (2) that the electron temperature $T_e$ term, residing in the exponential expression, provides a more efficient means for increasing the ionization probability as compared to linearly dependant $n_e$. The main factor that determines $T_e$ in plasma is the sputtering gas since there must be a sufficient number of high energy electrons to provide the needed ionization, i.e., above the ionization energy. This implies that gases with higher ionization energy than Ar ($E_i$ = 15.6 eV) such as He ($E_i$ = 24.58 eV) and Ne ($E_i$ = 21.56 eV) possess the potential to increase the electron temperature. In this work, Ne is used as the sputtering gas to utilize its higher ionization energy for increasing the electron temperature and, thus, explore its potential to increase ionization of C in a HiPIMS discharge. The choice of Ne over He is based on the higher sputtering yield of Ne for carbon [18].

HiPIMS is employed to achieve the largest possible electron density and, thus, further promote the tendency for electron impact ionization.

**2. Experimental Procedure**

Experiments were performed using a 50 mm diameter, 3 mm thick C target (purity 99.9%) in a high vacuum chamber (base pressure x$10^{-4}$ Pa). Power to the cathode was applied in the form of unipolar pulses. Pulses having a frequency of 600 Hz and a width of 25 μs were supplied by a pulsing unit fed by an MDX 1K direct current (DC) generator (Advanced Energy) operated at constant power of 40 W. Pure Ar and Ne discharges were compared using a gas pressure of 4.66 Pa under, otherwise, identical process conditions. The pressure of 4.66 Pa is relatively high compared to state-of-the-art values used for carbon sputtering which are in the order of 2 Pa [19]. It was difficult to generate plasma in a pure Ne atmosphere (at 2 Pa) due to the relatively high $E_i$ value of Ne. We successfully circumvented this issue (and performed depositions at 2 Pa) by carefully mixing Ar with Ne using an Ar-Ne gas mixture ranging from 0 % Ne to 83 % Ne. The effect of gas pressure and composition on the electron temperature was studied by recording time-resolved electron energy distribution functions (EEDFs) using a cylindrical Langmuir probe employing a procedure and a measurement setup described elsewhere [20,21]. Measurements were performed at a distance of 60 mm from the cathode and 60 μs after the pulse initiation (35 μs after the end of the pulse). The effect of the electron temperature on the ionization of C was investigated by measuring time-averaged $C^+$ ion energy distribution functions (IEDFs) using a target facing energy resolving quadruple mass spectrometer (PSM 003, Hiden Analytical). The contribution of the higher C sputtering efficiency of Ne in the $C^+$ ion intensity was investigated by measuring the mass deposition rates using a quartz crystal microbalance (QCM). To explore the feasibility of Ne-based HiPIMS discharge to synthesize dense and $sp^3$ rich amorphous carbon, thin films were deposited on water cooled Si substrates placed at a fixed substrate holder at 60 mm from the target. Depositions were performed by using pure Ar and 83 % Ne at 2 Pa and pure Ar and pure Ne at 4.66 Pa under, otherwise, identical conditions. A unipolar pulsed substrate bias with negative potentials ranging from 0 to 150 V and a frequency of 100 kHz was used during the film growth to control the energy of the ionized deposition flux. The densities of the grown films were determined by x-ray reflectometry (XRR) measurements performed with Cu-$K_{\alpha}$ ( $\lambda$ = 0.15406 nm) monochromatic radiation. The densities were calculated using the critical angle $\theta_c$ for the total external reflection [14]. In amorphous carbon films, the density is a direct measure of the $sp^3$ fraction given that the H content of the film is constant and below the threshold for hydrogenated amorphous carbon [13,14]. Therefore, we measured the hydrogen content of the grown films by time-of-flight elastic recoil detection analysis (ToF-ERDA).

**3. Results and Discussion**

In all recorded EEDFs, two electron populations (hereinafter referred to as cold and hot electrons) were observed [see the inset in Fig. 1(b) for an EEDF]; this is frequently encountered in HiPIMS discharges [20,22]. The temperature of the cold and hot electron populations — denoted as $T_{e\_cold}$ and $T_{e\_hot}$, respectively — are plotted as a function of the gas composition at the constant total pressure of 2 Pa [see Fig. 1(a)]. Mean ionization length ( $\lambda_{miz}$ ) is calculated using Eqs. (1) and (2), and is presented in Fig. 1(b). Due to similar behaviour with respect to the Ne content of the sputtering gas, $\lambda_{miz}$ only for $T_{e\_hot}$ is presented. It is observed that an increase of the Ne content in the gas atmosphere results in an increase in both $T_{e\_cold}$ and $T_{e\_hot}$. For $T_{e\_hot}$, this increase is about 76 % for the 83 % Ne case, at 2 Pa, and 55 % for the pure Ne case, at 4.66 Pa [not shown in Fig. 1(a)], compared to using only Ar at the same process pressures. The estimated reduction of $\lambda_{miz}$ is 88 % and 83 %, respectively. The corresponding decrease in $\lambda_{miz}$ using $T_{e\_cold}$ is 85 % and 96 %. It should be noted that aforementioned results refer to a time 35 μs after the end of the pulse. During the 35 μs, there is a decrease in the electron density and a cooling of the hot electrons by inelastic collisions [20]. Absolute values of the mean free paths used in our calculations will, therefore, be longer than during the pulse; in addition, the relative trends with gas mixture may be influenced. However, a global trend can be clearly seen; the efficiency of the carbon ionization as manifested by the decrease in the ionization mean free path [see Fig. 1(b)], is larger when sufficient Ne is present in the plasma, as compared to the pure Ar case.

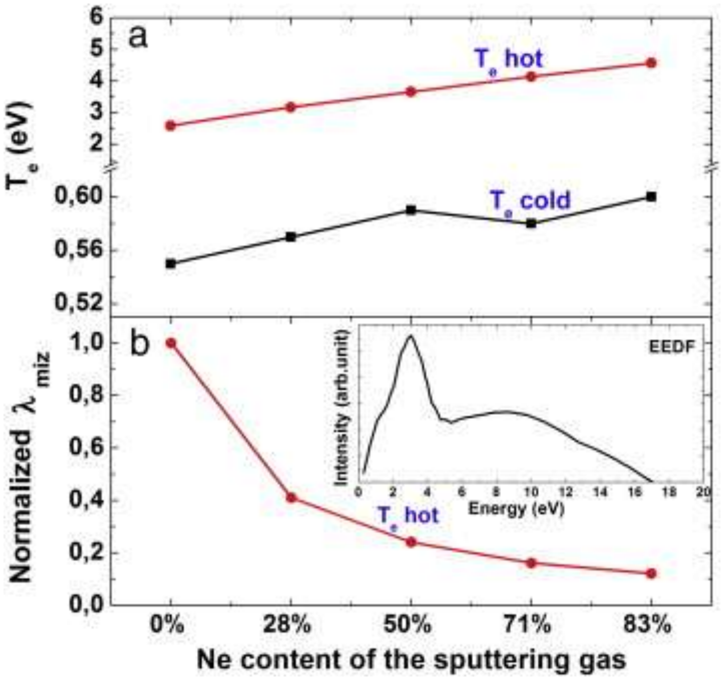


FIG. 1. (a) Average electron temperatures measured from hot and cold electron populations and (b) normalized ionization mean free path ( $\lambda_{miz}$ ) of $C^+$ ions calculated using Eq. (1) for different gas composition discharges. The error in the measurements is about 10%.

The IEDFs (presented in Fig. 2) exhibit an intense peak centred around 1 eV, corresponding to the thermalized population of ionized sputtered carbon and a high-energy peak indicating the presence of an energetic, ionized population of sputtered carbon. For sputtered material, the presence of a high-energy peak has previously been detected only for metals in high density discharges [23]. Intensity and position of the high-energy peaks of the IEDFs exhibit an increase with the increase in the Ne fraction. At 2 Pa, the highest Ne fraction (83%)

resulted in the most energetic high-energy population characterized by about eight times higher peak intensity as compared to pure Ar. For the same Ne content (83%), the total number of $C^+$ ions obtained by integrating IEDFs over energy is about 3 times larger. At the pressure of 4.66 Pa, the IEDFs from pure Ar and pure Ne show a trend similar to the IEDFs recorded at 2 Pa, but with a decreased high-energy peak due to the increasing amount of particle collisions at higher pressure. It should be noted that the measured mass deposition rates by QCM were found to increase not more than 20 % when changing the Ne content in the gas atmosphere from 0 to 83 %. The three-fold increase in the number of $C^+$ ions therefore, corresponds to a higher ion to neutral ratio in the case of Ne. Thus, the overall increase of the $C^+$ ion current with increasing Ne fraction clearly demonstrates that the degree of carbon ionization has increased.

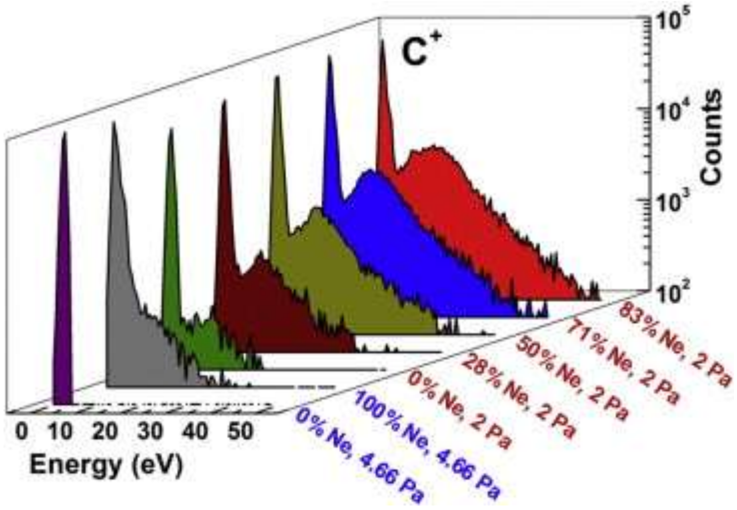


FIG. 2. The ion energy distributions for $C^+$ ions obtained from different gas composition discharges at the pressures of 2 Pa and 4.66 Pa.

Mass densities of the grown films are presented in Fig. 3. For the films grown at 2 Pa, the densities were found to increase with the increase in the negative substrate bias reaching its maximum at 100 V and decreasing thereafter. Films grown under the presence of Ne are, in general, denser as compared to those grown in a pure Ar atmosphere — except for the case when no bias is applied where no substantial difference is observed (both around 2 g/cm$^3$).

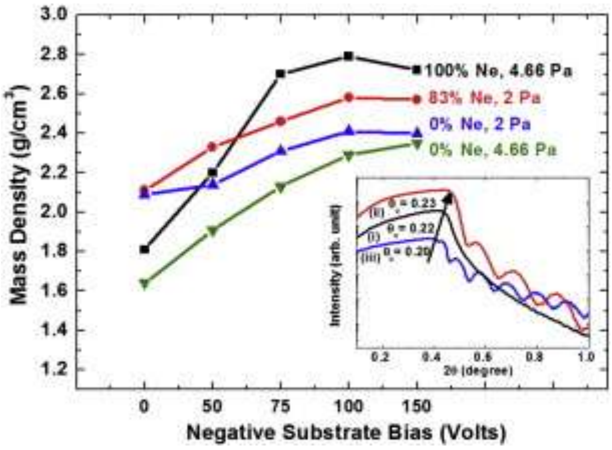


FIG. 3. Mass densities of carbon films; grown with different gas compositions at different substrate bias potentials. The inset shows representative XRR measured curves obtained for samples; i) Si substrate for the reference measurement, ii) 0% Ne at no substrate bias potential and iii) 83% Ne at a negative substrate bias potential of 100 V.

The maximum density obtained at 2 Pa for the 0% Ne case is 2.41 g/cm$^3$ while for the 83% Ne case it is 2.58 g/cm$^3$. At the higher pressure of 4.66 Pa, the maximum density values for 0 and 100% Ne are 2.3 and 2.8 g/cm$^3$, respectively. The densities are in good agreement with the achieved $C^+$ ion fluxes [see Fig. (2)] owing to the fact that high fluxes of $C^+$ ions – with energies sufficient to overcome the subplantation threshold – result in the increase in the local density, causing a bond rearrangement from graphite like ($sp^2$) to diamond like ($sp^3$) in the subsurface layers [13]. The hydrogen content in our films was found to be nearly constant in the range between 5 at.% and 10 at.%. These values are somewhat larger than those obtained in synthesis processes where H is not intentionally incorporated in carbon films [13]. A possible explanation for these findings may lie on the fact that depositions were performed in a high vacuum chamber (base pressure of the order of $10^{-4}$ Pa) that was not equipped with a load-lock chamber. Thus the deposition chamber had to be vented each time that a new substrate was loaded. This procedure is known to increase the water contamination of the chamber walls and may enhance the tendency of H incorporation into the growing film, especially in the case of relatively low growth rates as those used in our experiments. Moreover, the HiPIMS discharge, owing to its high density, may result in the generation of relatively large amount of activated radicals and atoms which may result in the incorporation of these species into the film increasing its H content [7]. However, irrespective of the level of H content in our films its nearly constant values imply that the observed density increase is a direct consequence of an increase in the C-C $sp^3$ bond fraction. As a comparison, the $sp^3/sp^2$ bond fraction obtained with FCVA and PLD approach 80-90% where the film densities range from 2.8-3.2 $g/cm^3$ [13]. We can therefore expect that our films with densities approaching 2.8 $g/cm^3$ are rich in C-C $sp^3$ bonds.

**4. Conclusions**

It has been shown that an increase in the degree of carbon ionization can be achieved in a HiPIMS discharge (via electron temperature enhancement) by using Ne, a gas with higher ionization energy than Ar. The direct consequence of the ionization enhancement on carbon growth was demonstrated by the resulting film density, which was found to reach 2.8 $g/cm^3$. In conclusion, the presented strategy opens up new perspectives on the implementation of magnetron sputtering based techniques for the synthesis of diamond like carbon and other carbon based materials.

**Acknowledgements**

The authors acknowledge Dr. Jens Jensen for ToF-ERDA measurements. The authors gratefully acknowledge the financial support provided by the Swedish Research Council (VR) through the contracts 621-2008-3222 and 623-2009-7348 and also for discussions within the COST Action MP0804 - HIPP Process.

**References**

[1] J. Bohlmark, M. Ostbye, M. Lattemann, H. Ljungcrantz, T. Rosell, U. Helmersson, Guiding the deposition flux in an ionized magnetron discharge, Thin Solid Films. 515 (2006) 1928-1931.

[2] J. Hopwood, Ionized physical vapor deposition of integrated circuit interconnects, Physics of Plasmas. 5 (1998) 1624.

[3] I. Petrov, P.B. Barna, L. Hultman, J.E. Greene, Microstructural evolution during film growth, Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films. 21 (2003) S117.

[4] U. Helmersson, M. Lattemann, J. Bohlmark, A. Ehiasarian, J. Gudmundsson, Ionized physical vapor deposition (IPVD): A review of technology and applications, Thin Solid Films. 513 (2006) 1-24.

[5] J.A. Hopwood (Ed.), Ionized Physical Vapor Deposition, Academic Press, San Diego, 2000.

[6] K. Sarakinos, J. Alami, S. Konstantinidis, High power pulsed magnetron sputtering: A review on scientific and engineering state of the art, Surface and Coatings Technology. 204 (2010) 1661-1684.

[7] K. Sarakinos, A. Braun, C. Zilkens, S. Mráz, J.M. Schneider, H. Zoubos, et al., Exploring the potential of high power impulse magnetron sputtering for growth of diamond-like carbon films, Surface and Coatings Technology. (2011). doi:10.1016/j.surfcoat.2011.11.032

[8] B.M. DeKoven, P.R. Ward, R.E. Weiss, D.J. Christie, R.A. Scholl, W.D. Sproul, F. Tomasel, A. Anders, in: S.o.V. Coaters (Ed.), 46th Annual Technical Conference San Francisco, CA, USA, 2003, p. 158.

[9] G. Aichmayr, a Avellan, G.S. Duesberg, F. Kreupl, S. Kudelka, M. Liebau, et al., Carbon / high-k Trench Capacitor for the 40nm DRAM Generation, 2007 IEEE Symposium on VLSI Technology. 49 (2007) 186-187.

[10] A.C. Ferrari, Diamond-like carbon for magnetic storage disks, Surface and Coatings Technology. 180-181 (2004) 190-206.

[11] C. Casiraghi, J. Robertson, A.C. Ferrari, Diamond-like Carbon for Data and Beer Storage, Mater. Today, 10 (2007) 44-53.

[12] H. Zhu, J. Wei, K. Wang, D. Wu, Applications of carbon materials in photovoltaic solar cells, Solar Energy Materials and Solar Cells. 93 (2009) 1461-1470.

[13] J. Robertson, Diamond-like amorphous carbon, Materials Science and Engineering: R: Reports. 37 (2002) 129-281.

[14] A. C. Ferrari, A. Libassi, B. Tanner, V. Stolojan, J. Yuan, L. Brown, et al., Density, sp3 fraction, and cross-sectional structure of amorphous carbon films determined by x-ray reflectivity and electron energy-loss spectroscopy, Physical Review B. 62 (2000) 11089-11103.

[15] C. A. Charitidis, Nanomechanical and nanotribological properties of carbon-based thin films: A review, International Journal of Refractory Metals and Hard Materials. 28 (2010) 51-70.

[16] M.H. Lee, C.W. Chung, Self-consistent global model with multi-step ionizations in inductively coupled plasmas, Physics of Plasmas. 12 (2005) 073501.

[17] R.S. Freund, C. Robert, R.J. Shul, T.R. Hayes, T. Laboratories, M. Hill, for electron-impact, Physical Review. 41 (1990) 3575.

[18] E. Oyarzabal, R.P. Doerner, M. Shimada, G.R. Tynan, Carbon atom and cluster sputtering under low-energy noble gas plasma bombardment, Journal of Applied Physics. 104 (2008) 043305.

[19] S. Logothetidis, A new process for the development of hard and stable sputtered amorphous carbon films, Vacuum. 53 (1999) 61-65.

[20] J.T. Gudmundsson, P. Sigurjonsson, P. Larsson, D. Lundin, U. Helmersson, On the electron energy in the high power impulse magnetron sputtering discharge, Journal of Applied Physics. 105 (2009) 123302.

[21] A. Aijaz, D. Lundin, P. Larsson, U. Helmersson, Dual-magnetron open field sputtering system for sideways deposition of thin films, Surface and Coatings Technology. 204 (2010) 2165-2169.

[22] J.T. Gudmundsson, J. Alami, U. Helmersson, Evolution of the electron energy distribution and plasma parameters in a pulsed magnetron discharge, Applied Physics Letters. 78 (2001) 3427.

[23] J. Bohlmark, M. Lattemann, J. Gudmundsson, a Ehiasarian, Y. Arandagonzalvo, N. Brenning, et al., The ion energy distributions and ion flux composition from a high power impulse magnetron sputtering discharge, Thin Solid Films. 515 (2006) 1522-1526.