CF_x films synthesized by reactive high power impulse magnetron sputtering of carbon in argon/tetrafluoromethane (Ar/CF_4) and argon/octafluorocyclobutane ($Ar/c\text{-}C_4F_8$) atmosphere

The synthesis of amorphous CF_x thin films by reactive high power impulse magnetron sputtering (rHiPIMS) was demonstrated in tetrafluoromethane and octafluorocyclobutane atmospheres. All depositions and the plasma characterization by positive ion mass spectrometry (Hiden EQP 1000, Hiden Analytical Ltd., UK) were carried out in an industrial coater (CC 800/9ML, CemeCon AG, Germany) utilizing a substrate temperature of 110ºC and a process pressure of 400 mPa. The CF_x film composition as measured by elastic recoil detection analysis was varied in the range of $0.15 < x < 0.35$ by regulating the partial pressure of the F-containing gases from 0 mPa to 110 mPa. Results from process and plasma characterization were related to *ab initio* calculations and CF_x thin film properties. Our DFT calculations predicted CF, CF_2, CF_3, as well as C_2 and F to be the most important precursor species for the film growth in Ar/CF_4 mixtures. For carbon discharges in Ar/C_4F_8 mixtures, additionally, C_2F_2 was predicted to play a significant role. Results obtained from time averaged positive ion mass spectrometry agree well with our theoretical calculations. Here, Ar^+, C^+, CF^+, CF_2^+, CF_3^+, as well as F^+ were found to be abundant cations (cf. figure 1 a) and b)). The characterization of the rHiPIMS processes revealed moreover two deposition regimes depending on the partial pressure of the F-containing reactive gas; as the partial pressure rises above 42 mPa in Ar/CF_4 plasmas an ionization cascade progresses, resulting in a rising peak target current and an increased formation of CF_4 fragments, especially CF_3. In C_4F_8 plasmas the ionization cascade onset was observed for partial pressures above 11 mPa, accompanied with an increased production of CF. These two regimes are mirrored in the thin film properties, particularly in their chemical bond structure, hardness and elastic modulus. The mechanical response of the CF_x films can also be related to abundant precursor ions in the plasma; in

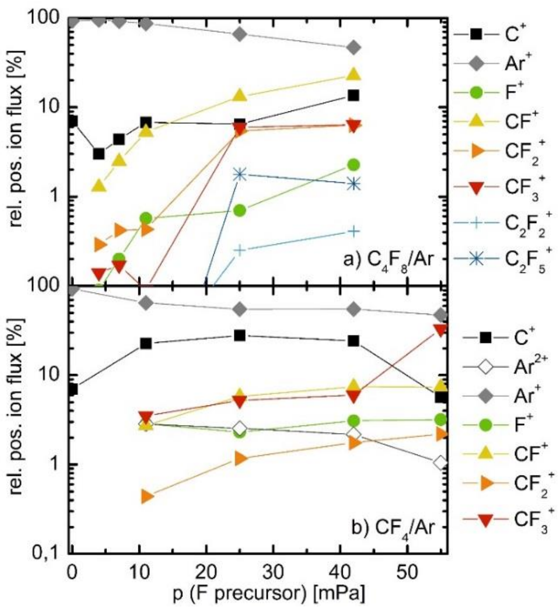

Figure 1 a) and b): Relative ion fluxes as a function of the reactive gas partial pressure for discharges in a) Ar/C_4F_8 and b) Ar/CF_4 extracted from time averaged IEDFs of corresponding processes.

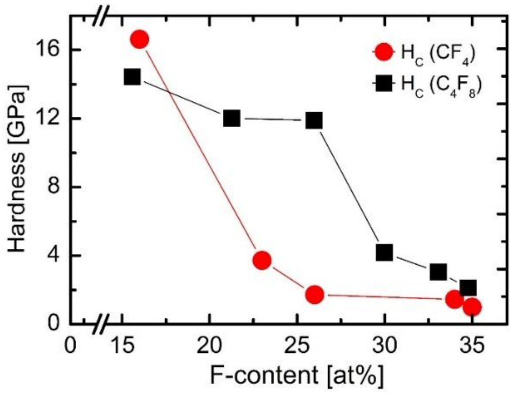

Figure 2: Hardness over the fluorine content for CF_x films grown in Ar/C_4F_8 (black squares) and Ar/CF_4 (red circles).

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C_4F_8 discharges next to Ar^+ and C^+, CF^+ species are most abundant. CF^+ and CF possess three dangling bonds, and are consequently reactive as well as able to build strong cross links in the carbon matrix. Therefore, CF_x films deposited in C_4F_8 show an elevated hardness over a wider range of incorporated F (cf. figure 2). In contrast, for Ar /CF_4 discharges CF_3^+ was determined as the species of highest abundance. CF_3^+ and its neutral counterpart have one dangling bond and thus does not significantly contribute to cross linking of the growing film. This is mirrored in a rapid decrease of the hardness as the F content in the films increases. Therefore, it can be concluded that the use of C_4F_8 has advantages with regards to the controllability of the film properties, while CF_4 covers a wide range of the applicable process window - thin film deposition and etching. Additionally, the dissociation of CF_4 into primarily CF_3 and F can be utilized for surface treatments and surface termination leading to low surface energies. Consequently, the rHiPIMS processes in C_4F_8 or CF_4 present a versatile tool for the further functionalization of carbon and carbon based thin films as well as surfaces.

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