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M. Weiler, K. Lang, E. Li, and J. Robertson

Deposition of tetrahedral hydrogenated amorphous carbon using a novel electron cyclotron wave resonance reactor

M. Weiler[a)]
Research Centre Rossendorf, Institute of Ion Beam Physics and Material Research, D-01314 Dresden, Germany

K. Lang
CCR GmbH, Beschichtungstechnologie, TZO Rheinbreitbach Maarweg 30, D-53619 Rheinbreitbach, Germany

E. Li
Akashic Memories Corporation, San Jose, California 95134

J. Robertson
Department of Engineering, Cambridge University, CB2 1PZ, United Kingdom

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Highly tetrahedral hydrogenated amorphous carbon (ta-C:H) is deposited with a novel, 13.6 MHz excited electron cyclotron wave resonance (ECWR) plasma source. The ion flux of an acetylene and a nitrogen plasma was investigated by mass spectrometry and retarding field measurements. The ECWR gives a dissociation degree between 15% and 80% depending on gas flow rate. Ion current densities up to 2 mA/cm^2 can be achieved, corresponding to ta-C:H deposition rates of 2 nm/s. The fraction of sp^3 bonded carbon atoms and mass density are strongly related to the amount of hydrogen in the ion flux. For low hydrogen ion fluxes (10%), a sp^3 fraction of 70% and a mass density of 2.85 g/cm^3 can be achieved. At higher hydrogen ion fluxes (40%), the sp^3 fraction and the mass density fall to 55% and 2.55 gm/cm^3, respectively. © *1998 American Institute of Physics.* [S0003-6951(98)02251-1]

There is presently great interest in plasma sources with well defined, low energy ion fluxes for thin film deposition and plasma etching. The deposition of hard coatings such as diamondlike carbon or cubic boron nitride requires highly ionized beams of the appropriate species at about 100 eV in energy.[1–5] Similarly, insulating films of silicon nitride and silicon dioxide grown at low temperatures are improved if the films are grown from energetic species as this minimizes the hydrogen content.[6,7] Ideally, these applications require a plasma source with a high plasma density, a well defined ion energy, and an independent control of the ion energy and the ion current. Electron cyclotron resonance (ECR) sources. satisfy many of these requirements but they use microwaves. There is an advantage to use sources with radio frequency excitation, as this is easier to handle and scale up.

This letter describes a novel electron cyclotron wave resonance (ECWR) controlled plasma reactor (COPRA) in which the ion current density, ion energy, and the degree of ionization or dissociation can be controlled independently of each other, over a wide range. The COPRA is a single-turn inductively coupled rf (13.6 MHz) discharge with a superimposed static transverse magnetic field. The ion energy can be varied by applying a rf bias voltage to an electrode placed behind the plasma ball. The operation of the COPRA was characterized by ion flux measurements as a function of rf power, gas flow rate, and magnetic field, using hydrogen, nitrogen, oxygen, and acetylene as working gases. A set of conditions was found which gives 80% dissociation of molecular hydrogen, oxygen, and nitrogen. This is of great technological importance for the deposition of silicon dioxide, silicon nitride, boron nitride, and even diamond.

Capacitively coupled rf sources used in plasma enhanced chemical vapor deposition give a relatively low plasma density because of the inefficient coupling of rf power to the plasma. In the ECWR, the transverse magnetic field produces two circularly polarized waves, one of which becomes resonantly coupled to the plasma (see Refs. 8–12). A typical experimental setup can be found in Ref. 11. This ECW resonance leads to a strong absorption of energy from the rf and a high plasma density of order 10^{13} cm^{-3}, even for 13.6 MHz excitation. Figure 1 shows the variation of the ion current density of a C_2H_2 plasma as a function of the normalized magnetic field strength $\beta=\omega_c/\omega$ ($\omega_c=(e_0/m)B_0$, $\omega=2\pi 13.6$ MHz) at a plasma chamber pressure of 5×10^{-4} mbar. The curve in Fig. 1 is characteristic for this source; i.e., for various working gases and over a pressure range from 2×10^{-4} to 2×10^{-3} mbar it displays a shoulder and a strong resonance (here at $\beta\cong3.3$). The latter is related to the zero order ECW resonance according to Pfeiffer[9] and Oechsner.[11]

The operation of the COPRA was first tested using nitrogen as the working gas. The ion flux composition was analyzed by mass spectrometry using a Hiden EQP300 plasma monitoring system. The transmission function of the EQP300 was calibrated by retarding field Faraday cup measurements. For diatomic gases like oxygen, nitrogen, and hydrogen, a dissociation degree of nearly 80% can be achieved

[a)]New address: CCR GmbH, Beschichtungstechnologie, Maarweg 30, D-53619 Rheinbreitbach.

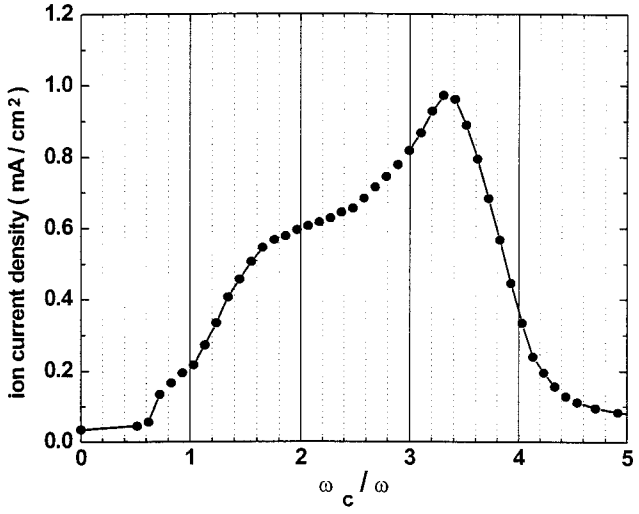

FIG. 1. Variation of the ion current density as a function of the normalized magnetic field strength.

in the zero order ECW resonance. For example, Fig. 2 shows the fraction of atomic nitrogen ions in the ion flux of a nitrogen plasma ranging from 0.15 ± 0.1 to 0.8 ± 0.2 by varying the nitrogen gas flow between 10 and 45 sccm. The results in Fig. 2 were obtained for a fixed pumping speed of 1000 ℓ/s and fixed rf power of 200 W. Under these conditions, the nitrogen gas pressure in the plasma chamber ranges from 0.2×10^{-3} mbar at a flow rate of 10 sccm up to 1.2×10^{-3} mbar at a flow rate of 50 sccm. Similar results were obtained for oxygen and hydrogen. The high dissociation of 80% clearly demonstrates the advantage of ECWR excitation over even microwave ECR, where the atomic nitrogen fraction normally does not exceed 20%–30%.[13]

The dissociation degree is expected to depend strongly on the residence time in the plasma, and this depends on gas flow rate, pumping speed, and gas pressure. The dependence on residence time is well known for a low pressure plasma[14] and arises from a competition between the formation of atomic N by electron collision dissociation and the diffusional loss to the chamber walls. Direct three-particle recombination can be neglected at such low pressure plasmas, so that the strong increase in the fraction of atomic nitrogen seen in Fig. 2 must arise from lower diffusion losses due to elastic collisions at higher gas pressures.

Figure 2 shows that the source can provide almost pure

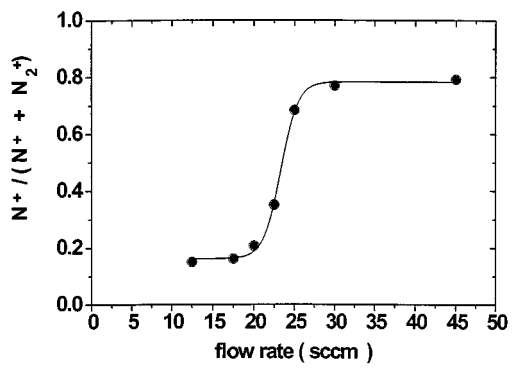

FIG. 2. Fraction of atomic nitrogen as a function of the gas flow rate.

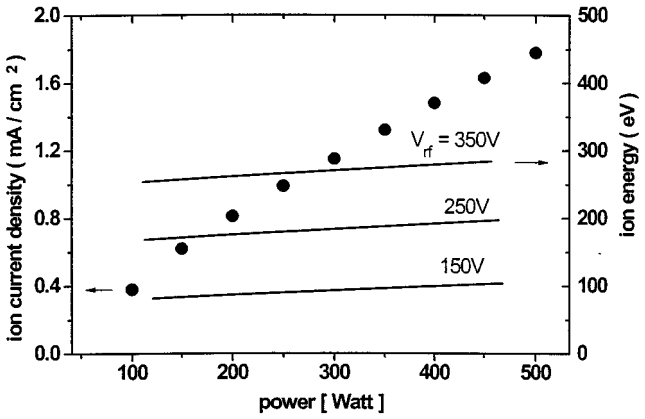

FIG. 3. Variation of ion current density (at fixed rf amplitude of 150 V, dotted line) and ion energy (at fixed rf amplitudes of 150, 250, and 350 V, continous lines) for a C_2H_2 plasma as a function of rf power.

plasma beams of either N_2^+ or N^+. The ion current density of N^+ and N_2^+ can be varied between 0.1 and 1.5 mA/cm^2 by varying the rf power from 100 to 500 W in the zero order resonance. The COPRA represents a pure inductively coupled plasma where the ion energy is given by the plasma floating potential of about 20 V at pressures of 0.2×10^{-3}–1.2×10^{-3} mbar. The ion energy distribution always is a sharp Gaussian with a width $\Delta E/E$ of below 5%. The mean ion energy can be varied from 20 to 300 V by applying an additional rf bias voltage[15] to an electrode behind the plasma ball. Varying the plasma potential does not alter the plasma density in this source, so the ion current does not change. Furthermore, changing the plasma density by varying the rf power causes only small variations in the plasma potential, and therefore the ion energy is nearly constant over a wide range of ion current densities. This independent control of ion current density and ion energy is displayed in Fig. 3 for a C_2H_2 ion beam. The ion current density varies between 0.15 and 2 mA/cm^2 for increasing rf power and the ion energy is determined mainly by the bias voltage as shown in Fig. 3 for three different rf bias voltages.

The COPRA source has been used to deposit a highly sp^3 bonded form of diamondlike carbon called *ta*-C:H using an acetylene plasma beam. We previously deposited *ta*-C:H using a plasma beam source (PBS).[16,17] The PBS gave a high sp^3 bonding in ta-C:H because it satisfied three conditions; a highly ionized plasma beam, a single ion species, and a sharp ion energy spectrum centered around 200 eV, which corresponds to about 100 eV per C atom. The COPRA improves on the PBS in three ways; it provides a factor 10 higher growth rate to a commercially useful value, it allows the independent electrical control of the ion current and ion energy, and it allows low ion energies to be accessible. The latter is useful as this allows higher substrate temperatures to be used before sp^2 bonding occurs.[18]

The ion flux in the PBS consists mainly of C_2H_2 ions and with negligible amounts of hydrogen and other CH radical ions.[17] A similar dissociation pattern of C_2H_2 was expected in the ECWR. In fact, analysis of the ion flux of a acetylene plasma finds a lower degree of dissociation in that of a nitrogen plasma. The ion mass spectrum contains mainly $C_2H_2^+$, C_2H^+, H^+, and H_2^+ ions, with the ratio of hydrogen

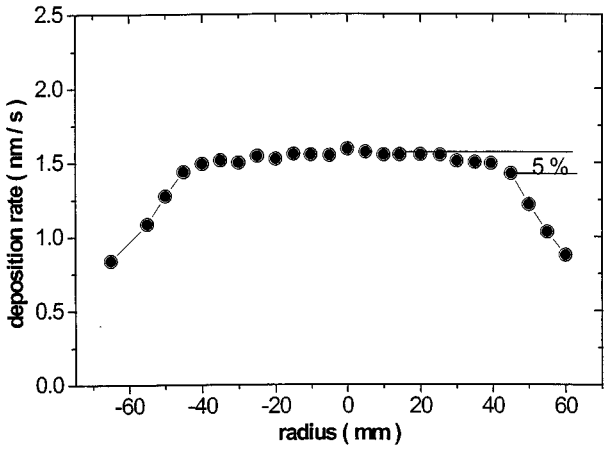

FIG. 4. Radial distribution of deposition rate for *ta*-C:H deposition.

ions to the total ion flux varying from 0.2 to 0.5, depending on gas flow rate. This arises from the weak dependence of pressure on gas flow rate. The total pressure reaches only 5. for gas flow rates of 10–50 sccm due to a strong gettering effect of radicals at the surface of the plasma reactor walls.

Ta-C:H films were deposited at three different flow rates corresponding to 10%, 20%, and 40% of hydrogen ions in the total ion flux. The ion energy and ion current density were kept constant during each deposition at 200 ± 10 eV and 1.5 mA/cm^2 ($P = 400$ W), respectively. The films were deposited on 125 mm diameter (100) silicon wafers. Figure 4 shows that the radial homogeneity of the deposition rate is within 5% over the wafer diameter. The deposition rate is strongly related to ion current density. For 1.5 mA/cm^2 a deposition rate of 1.5 ± 0.1 nm/s is found, ten times higher than achieved with the PBS.

The microscopic density and sp^3/sp^2 fraction were determined by electron energy loss spectroscopy (EELS), as summarized in Table I. The density is derived from the valence plasmon energy and the sp^2/sp^3 bonding fraction was derived by analyzing the carbon *K*-edge spectrum as described earlier.[17] Deposition from a beam with low hydrogen ratio in the ion flux gives a mass density of 2.85 g/cm^3 and an sp^3 fraction of 70%. Using nanoindentendation and spectroscopic ellipsometry a hardness of about 60 GPa and a refractive index of 2.5 is obtained, similar to results of films produced by the PBS.

TABLE I. EELS results.

Flow rate (sccm)	H_x^+/H_x^+ ($C_2H_x^+$) (%)	Mass density (g/cm^3)	sp^3-content (%)
10	10	2.85	70
25	20	2.70	65
45	40	2.55	55

The sp^3 content and density fall for higher hydrogen ion fluxes. For 40% hydrogen in the ion flux, the mass density falls to 2.55 g/cm^3 and the sp^3 fraction is 55%. This behavior is consistent with the findings of von Keudell *et al.*,[19] who suggested that hydrogen ions create dangling bonds by displacement or chemical abstraction of hydrogen from the film. The dangling bonds then relax either by saturation by hydrogen bonding or by forming sp^2 bonds. These results show that gas flow rate—by changing the content of hydrogen in the ion flux—can also affect sp^3 fraction, a feature which did not arise in the PBS original work.

In conclusion, a novel ECWR controlled plasma beam source is presented which can provide almost pure plasma beams of either N_2^+ or N^+ ions with ion current densities up to 2 mA/cm^2. The source gives large area deposition of a *ta*-C:H from acetylene, with high deposition rates of up to 2 nm/s.

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