Properties of Amorphous Carbon Films

Introduction

The properties of hydrogenated amorphous carbon (a-C:H) films have been studied over the past decade. A broad spectrum of applications ranging from carbon-based semiconductors, to wear-resistant coatings, to corrosion-resistant surfaces, to coatings on microspheres for inertial confinement targets has been identified. Plasma-based deposition systems use several approaches to decompose the feed gas and grow the carbon films: radio frequencies,[1] direct currents,[2] hot filaments,[3] glow discharges, and saddle fields.[4] In saddle-field plasmas, electrons oscillate between two electrodes to ionize the feed gas. Ions are drawn from the plasma by a gentle axial field and are delivered to a substrate beyond the transparent electrodes. Ions, radicals, and neutrals participate in the film growth process.

The underlying strength of the saddle-field plasma configuration rests in the ability to control several plasma parameters independently over a broad range of operating conditions and to deposit films outside the plasma region. The ion flux and energy, the ratio of the charged particles to neutral particles leaving the plasma, the temperature of the substrate, and the chemical species being deposited on the substrate can be tailored to optimize film properties for specific applications. Adjusting these parameters can alter the film density, the hydrogen content, the intrinsic stress within the films, the porosity, and the surface morphology.

To understand how deposition conditions influence the film properties—stress, density, and growth rate—a series of thin films were grown on flat glass and Pyrex™ plates. The correlation between film stress and deposition condition was measured by coating 0.1-mm-thick glass substrates with a-C:H and measuring the resultant curvature of the bilayer. Density and growth rate were measured by depositing films on thick Pyrex™ plates that were masked with stainless steel covers with an 18.9-mm-diam hole near the center. Subsequently, films were grown on polyalpha-methylstyrene (P*a*MS) and glow discharge polymer (GDP) microspheres using the conditions established for flat plates. One motivation for this work was to establish a protocol for coating microspheres with thick, smooth, high-density hydrogenated amorphous carbon films for the inertial confinement energy program as a precursor to growing tritiated films. This paper summarizes the film properties that were obtained and discusses their dependence on deposition conditions.

Film Properties

The deposition chamber used in this work is a right cylinder. Stainless steel was the construction material of choice. A transparent anode grid divides the deposition chamber in half. Transparent grid cathodes are located 15 cm from the anode at either end of the cylinder. Electrically floated end plates are positioned approximately 7 cm beyond the cathodes. The grid open area is approximately 80%. Substrates to be coated are fixed to the end plates.

Each substrate was cleaned and degreased in an ultrasonic bath using trichloroethylene, acetone, and methanol in sequence. The substrates were then rinsed with de-ionized water, dried, and fixed on the end plate. All depositions were carried out at or near room temperature. Internal components in the vacuum chamber were inspected, removed, and cleaned before each run. Immediately following a deposition, the film thickness and the radius of curvature of the coated thin substrate were measured using a profilometer. The surface morphology was examined under an optical microscope. The films were subsequently stored in air for more detailed examination. Surfaces were inspected daily under the optical microscope for changes. The structure of the film was examined by breaking the coated substrates to view its cross section under a high-resolution scanning electron microscope (SEM). Thickness was measured using both profilometry and SEM. Film density was estimated from profilometry and SEM data.

Surface Condition

The surface smoothness of films bonded to Pyrex™ substrates depended on the deposition conditions but did not change with time once the deposition was completed. In general, particulate deposition increased with increasing methane pressure. The roughest films were produced at 27 Pa, the

smoothest at 1.3 Pa. Film smoothness could be further enhanced with hydrogen dilution of the methane plasma.

Films deposited on P*a*MS microspheres tended to detach from the underlying structure over the course of several days. Figure 89.39 illustrates typical ridges that evolved and stabilized on a P*a*MS shell over 28 days. No deposition conditions for pure methane plasmas could be found to increase the film–substrate bonding to the level that prevented film detachment on P*a*MS shells. Detachment, however, was never observed on GDP microspheres or Pyrex™ substrates even in pure methane plasmas.

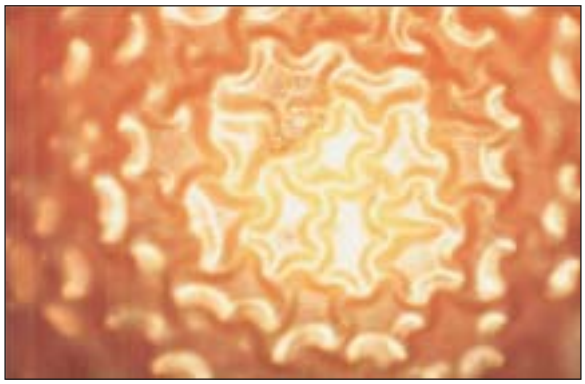

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Figure 89.39
Surface morphology on a P*a*MS microsphere 28 days after deposition; methane pressure: 5.3 Pa, flow rate: 3.5 sccm, anode current: 30 mA, floated substrate.

Film Cross Sections

A typical film cross section using SEM is provided in Fig. 89.40. The film, on the right-hand side of the picture, is intimately bonded to the Pyrex™ substrate. The body of the film is devoid of any microstructure, even at SEM resolutions on the 10-nm scale; these films are amorphous. As the deposition proceeds, the film grows with the agglomeration of matter on the surface coalescing into the uniformly dense and featureless layer seen in this figure. Several types of particles are involved in the growth process: fragmented methane comprising neutrals and radicals with varying CH atom ratios, including C and H atoms; more-complex CH chains that have polymerized in the plasma; and solid particles that have dislodged from chamber surfaces and attached to the film surface. The relative contributions of these components condensing on the surface to the film growth dynamics depend more on hydrogen dilution of the methane plasma than on the operating methane pressure. Films grown in pure methane plasmas exhibit surface roughness and porosity that are unacceptable for microsphere applications. Surface smoothness improves, however, when the methane is diluted with hydrogen, and increasing dilution increases surface smoothness.

Hydrogen dilution has additional effects. Plasma stability improves with dilution. There is a notable lack of carbonaceous deposition on the grids and chamber walls. Undiluted methane plasmas are responsible for particulate agglomeration in the gas phase and particle production that eventually find their way to the film surface.

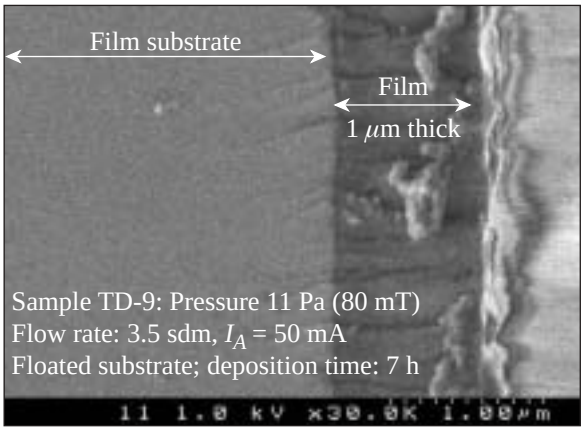

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Figure 89.40
Typical film cross section using SEM; methane pressure: 11 Pa, flow rate: 3.5 sccm, anode current: 50 mA, floated substrate.

Internal Stress

The relative intrinsic stress within the films can be estimated from the radius of curvature of the coated thin wafers.[5,6] The larger the curvature of radius, the lower the relative intrinsic film stress. The relative stress dependence on fill pressure and methane concentration for several films is provided in Figs. 89.41 and 89.42, respectively. All data have been scaled to a uniform film thickness of 1 *m*m for this comparison.

Figure 89.41 indicates that roughly doubling the deposition gas pressure from 2.7 Pa to 5.3 Pa reduces the relative stress approximately fivefold. At an operating pressure of 25 Pa, film stress approaches zero. At the higher operating pressures, plasma particles impinging on the film surface have lower impact energies. They are less likely to embed into the film

bulk. Under these conditions, films grow by particle condensation on the surface rather than by implantation into the bulk. These films can readjust during the growth process to reduce internal stress.

Figure 89.42 illustrates that stress in films increases as the fraction of hydrogen in H_2/CH_4 plasmas decreases and exceeds values for films grown in undiluted methane plasmas. The transition to lower stress values in pure methane plasmas most likely reflects the difference in the plasma composition between diluted and undiluted plasmas.

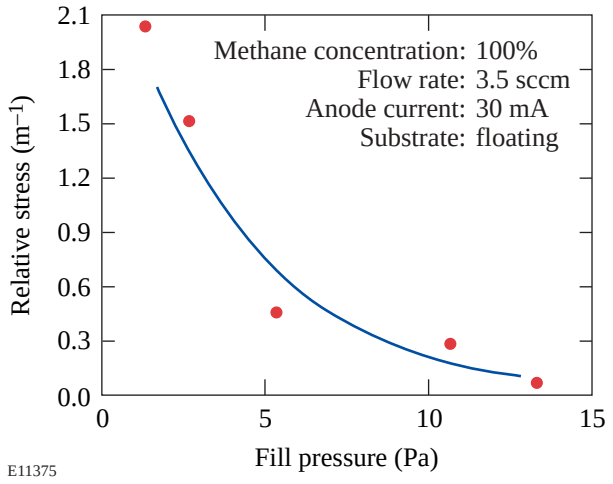

Figure 89.41
Stress in hydrogenated films decreases with increasing methane pressure.

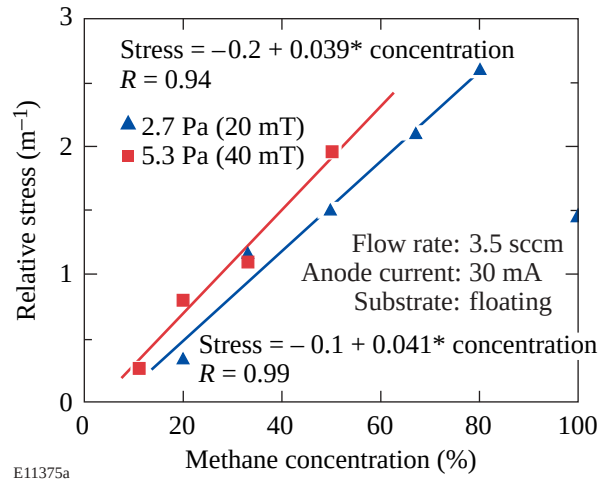

Figure 89.42
Stress in hydrogenated films increases with decreasing dilution of the methane plasma.

Thickness and Density

Densities are derived from the thickness of the film deposited on the substrate through a stainless steel mask and the film weight determined by weighing each substrate before and after deposition. Film thickness has been measured using both profilometry and SEM. A variation in the film thickness across the diameter of the mask resulting from a shadowing effect by the mask has been included in the density calculation. The film thickness along the border of the mask is smaller than in the center of the opening. Thickness and density estimates based on SEM data are considered to be more reliable and consequently used throughout this discussion.

Figure 89.43 illustrates that film density is strongly dependent on pressure, decreasing with increasing neutral pressure. At lower neutral pressures the electron temperature in the plasma is higher. Higher-energy electrons decompose a larger proportion of the feed gas into smaller neutrals, radicals, and ions. When these particles condense on the substrate, they tend to form higher-density, diamond-like films rather than lower-density, polymeric-like films.

Figure 89.44 demonstrates that film density is also weakly dependent on methane concentration in the plasma, in general increasing with decreasing hydrogen dilution. Increasing the methane concentration in the plasma for a fixed neutral pressure increases the carbon flux to the substrate relative to the hydrogen flux and leads to higher-density films. At 20%

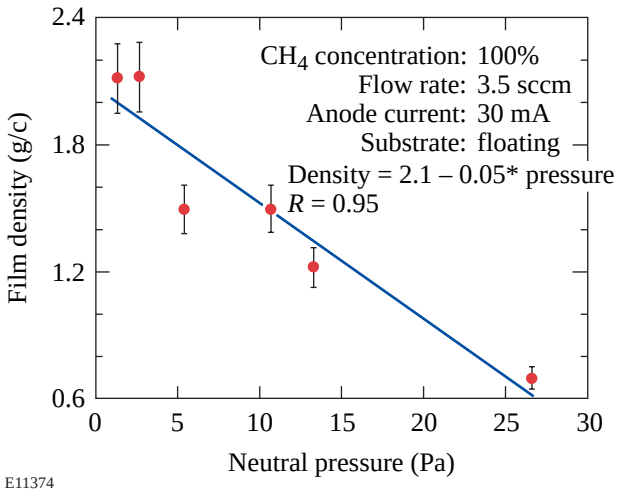

Figure 89.43
Hydrogenated film density decreases with increasing methane pressure in the deposition chamber.

methane, the atom C/H ratio is 8%; at 80% that ratio increases to 22%. The plasma is predominantly a hydrogen plasma with an increasing minority constituent as the methane concentration increases. It is noteworthy that up to 80% methane concentration, film densities for both neutral pressures are similar, suggesting that the plasma properties are similar for the two cases. At 100% the C/H ratio is 25%; however, the lower operating pressure, 2.7 Pa, yields a film with a significantly higher density than for the 5.3-Pa case, suggesting that the plasma properties for that case are very different.

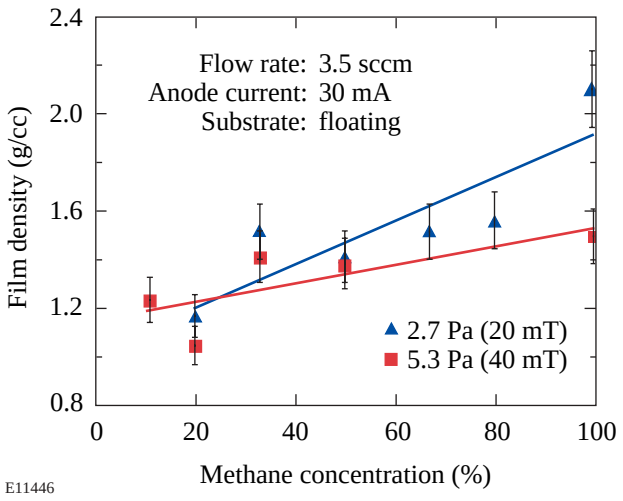

Figure 89.44
Film's density's dependence on hydrogen dilution of the methane.

Growth Rate

Growth rate depends on the operating pressure, as illustrated in Fig. 89.45. It peaks near 5 Pa and decreases at both lower pressures and higher fill pressures. At pressures below 5 Pa, the number of carbon atoms present in the plasma limits the film's growth rate. The extraction rate is fixed by the electric field within the plasma sheath, so the film can grow only at the rate that carbon species enter the sheath from the plasma side. The carbon particle density is determined by the fill pressure. Increasing the fill pressure increases the number of carbon species available for film growth, as the figure illustrates. At pressures above 5 Pa the growth rate is reduced because the extraction field strength is reduced at the higher fill pressures. While the carbon species density in the plasma is high, most of these particles are not available for film growth. The peak near 5 Pa represents the optimum balance between available carbon species in the plasma and their extraction rate for this system.

Figure 89.46 illustrates the film's growth rate dependence on methane concentration at a fixed neutral pressure. Fixing neutral pressure fixes the extraction field. Increasing the carbon species number density within the plasma by increasing the methane concentration also increases the number of particles available for extraction. The extraction rate and consequently the growth rates are seen to increase with methane concentration in this figure as expected.

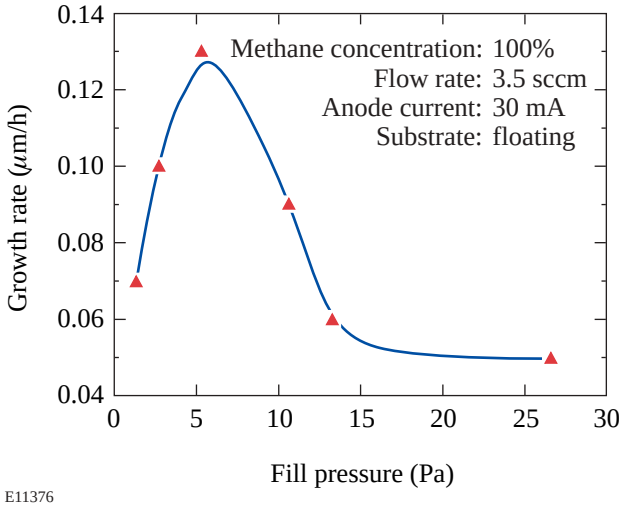

Figure 89.45
Growth rate dependence on neutral pressure.

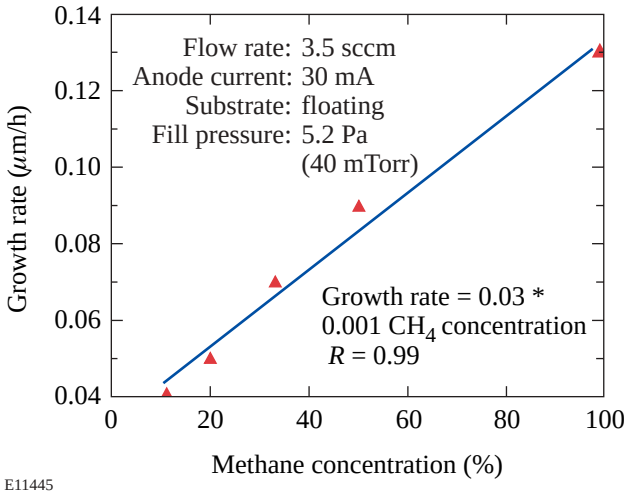

Figure 89.46
Growth rate increases with increasing methane content in the plasma.

Conclusions

The surface morphology of films depends on the operating gas pressure and the hydrogen concentration in the gas mixture. Surface smoothness improves with decreasing gas pressure and increasing hydrogen dilution. Gross features on the surfaces, such as lumps and pits, are attributed to particulate transport from the plasma to the film surface. Film chips detached from the chamber walls are the most likely source of these particles. The presence of hydrogen reduces the production or existence of larger-chained molecules in the plasma. Consequently the deposition of these particles on the films, the grids, and the walls is strongly suppressed. Fine structure on the film surface is attributed to the deposition conditions—the energy of the impacting particles, the ratio of the atom/neutral/radical fluxes, and the magnitude of the carbon flux—and is most likely related to gas phase polymerization within the plasma.

Hydrogen dilution also improves plasma performance. Long-term plasma stability improves because the grids are not progressively coated with carbonaceous material.

The key deposition parameter responsible for residual stress in the film is the pressure of the precursor gas. Decreasing the pressure from 27 Pa to 1.3 Pa increases the residual stress in the films. Increasing the pressure of the precursor gas decreases the anode potential and increases the substrate self-bias, thereby changing the energy distribution of the particle flux involved in the deposition process.

Deposition of films on PαMS microspheres showed that stress generated during the growing process can drastically change the topology of the coated surface over time. In some cases changes began within a few hours of deposition, while in other cases the films were unaltered for several weeks. In addition to these time-dependent manifestations, all films exhibited a granular surface.

Operating pressure also plays an important role in modulating density and growth rate. Film density depends on the gas pressure. Film density increases with decreasing gas pressure to reach a maximum of 2 g/cc at 2.7 Pa in methane plasmas. Diluting the methane with hydrogen decreases the film density.

Growth rates up to 0.13 μm/h have been achieved. These tests provide the deposition conditions for growing tritiated amorphous carbon films.

ACKNOWLEDGMENT

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REFERENCES

1. S. R. P. Silva *et al.*, Diam. Relat. Mater. **4**, 977 (1995).
2. D. S. Whitmell and R. Williamson, Thin Solid Films **35**, 255 (1976).
3. E. N. Farabaugh *et al.*, in *Applications of Diamond Films and Related Materials: Third International Conference*, edited by A. Feldman *et al.* (NIST, Gaithersburg, MD, 1995), Vol. 1, pp. 361–364.
4. F. Gaspari *et al.*, in *Applications of Diamond Films and Related Materials: Third International Conference*, edited by A. Feldman *et al.* (NIST, Gaithersburg, MD, 1995), Vol. 1, pp. 743–746.
5. J. G. Kim and J. Yu, J. Mater. Res. **13**, 3027 (1998).
6. H. Yamada, O. Tsuji, and P. Wood, Thin Solid Films **270**, 220 (1995).