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Protective amorphous carbon coatings on glass substrates

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Thick amorphous carbon films were deposited by the Magnets-in-Motion (M-M) rf linear hollow cathode at varying acetylene contents in Ar in a hybrid PVD/PE-CVD process directly on glass substrates. The hollow cathode plates manufactured from graphite were used as the PVD target. The measurements show that the films can reach thickness of up to 50 µm at deposition rates of up to 2.5 µm/min. Scratch test measurements confirm that well adhering films several µm thick can be achieved at C₂H₂ contents of up to 0.5%. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5002091

I. INTRODUCTION

The amorphous carbon and diamond like carbon (DLC) thin films are widely used in industry because of their excellent properties. The applications include coatings of automotive parts, metal cutting inserts, razor blades, orthopedic implants, magnetic storage discs and their read heads. The applications require that the films are well adhered to the substrate. Poor adhesion is a common issue for non-metallic substrates, especially glass.

Substrate pretreatment methods for improving the adhesion on glass substrates are for example cleaning in an alcohol, alkali or acidic bath for a certain amount of time. A widely used method is employing carbide-forming interlayers. Good results have been reported for Si, CrC/C, Al and Ti interlayers. The method employed in this work was the Ar sputter-cleaning.

In this paper we present deposition of amorphous carbon films directly on glass substrates, without an interlayer, at different C₂H₂ contents in Ar carrier gas. The plasma deposition system uses the radio frequency (rf) Magnets-in-Motion (M-M) linear hollow cathode in the hybrid PVD/PE-CVD processes. The thick coatings, well adherent to glass, indicating short-range graphite order exhibited very similar Raman spectra as ultra-thin nano-graphitic adhesive pyrocarbon films (PCF) on silica. In Ref. 10 the depositions of amorphous carbon coatings on glass were performed at lower 9.3 Pa (0.07 Torr) and moderate 46.5 Pa (0.35 Torr) pressures. The results indicated that by using higher pressures and higher gas flows higher deposition rates could be achieved. Therefore, the pressure of 40 Pa (0.3 Torr) was used in this work. However, the gas mixing ratios had to be examined so that a good adhesion, matching the lower pressure results is achieved. Results from the optical emission spectroscopy and film properties at varying gas composition ratios, deposition rate and adhesion are presented and discussed.

II. EXPERIMENTAL

Deposition of the amorphous carbon films was carried out with the Magnets-in-Motion (M-M) radio frequency linear hollow cathode. Full description of the system was published elsewhere. The system comprises two parallel graphite cathode plates placed 45mm above the sample holder. The gas mixture (C₂H₂ and Ar) is introduced in between the cathode plates through a multiple nozzle system.
TABLE I. Deposition parameters for amorphous carbon films on glass substrates.

| Deposition method                          | Linear hollow cathode M-M hybrid PVD/PE-CVD |
|-------------------------------------------|---------------------------------------------|
| Distance between the cathode outlet and substrate | 45 mm                                      |
| Rf power                                  | 1200 W                                     |
| Substrate bias                            | 500 W                                      |
| Pressure in the deposition chamber        | 40 Pa (0.3 Torr)                           |
| Total Ar + C$_2$H$_2$ gas mix flowrate     | 1500 sccm                                  |
| C$_2$H$_2$ content in the mixture         | 0 to 3%                                    |
| Deposition time                           | 20 min                                     |

with nozzles placed uniformly along the cathode plates. To ensure that the ion density is uniform along the hollow cathode plates, two rotating NdFeB permanent magnets are positioned along the cathode plates. Two radio frequency power sources of 13.56 MHz were used to excite the plasma in the linear hollow cathode and to bias the sample holder. The system was equipped with a mechanical rotary pump and a Roots blower.

The amorphous carbon thin films were deposited on 1 mm thick, 2.5 × 7.5 cm$^2$ microscope glass slides. Pretreatment by Ar sputter-cleaning in rf plasma was employed prior the deposition.

The films were deposited at different acetylene (C$_2$H$_2$) mixing ratios with Ar. Thus, carbon was supplied both from the linear hollow cathode plates (PVD process) and from acetylene (PE-CVD process). The experiments were performed at the following C$_2$H$_2$ amounts in the gas mixture: 0%, 0.25%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5% and 3%. The rf power, pressure and bias were kept constant. The deposition parameters are summarized in Table I.

Following measurements were performed to analyze the deposited coatings and process: optical emission spectroscopy for process analysis, scanning electron microscopy (SEM) for evaluation of the film thickness and deposition rate and scratch tests for the adhesion analysis.

The optical emission spectra were recorded by PLASCALC-2000-UV-VIS-NIR Plasma Monitoring & Process Control System. Hydrogen atomic lines Hα and Hβ, CH 4300 Å system band (0,0) ($\lambda$ = 431.4 nm), CH 3900 Å system band (0,0) ($\lambda$ = 388.9 nm) and C$_2$ Swan system ((0,0), (1,1), (1,0) (2,1), (3,2), (4,3) bands) were detected.

The adhesion was analyzed by a scratch test according to the EN ISO 20502:2016 standard. At a progressive force operation mode, the loading force was increased from 0 up to 51 ± 0.05 N at a loading rate of 4.9 ± 0.11 N/mm. The adhesion was characterized by three critical load levels:

- **LC1** – failure of the cohesive strength - cracking of the coating at the edges of the scratch line;
- **LC2** – failure of the cohesive and adhesive strength - detachment of the coating from the substrate at the edges of the scratch line;
- **LC3** – failure of the adhesive strength - detachment of the coating from the substrate at the center of the scratch line.

For each sample 3 consecutive measurements were made and average LC1, LC2, LC3 values are reported for each sample.

III. RESULTS AND DISCUSSION

The optical emission spectrum from the discharge with 0.5% C$_2$H$_2$ in the gas mixture with Ar is shown in Fig. 1. It can be seen that both Hα (2-3 transition, $\lambda$ = 656.5 nm) and Hβ (2-4 transition, $\lambda$ = 486.1 nm) are present. From the C$_2$ Swan system, strong (0,0) and (1,1) bands as well as four weaker bands (1,0) (2,1), (3,2), (4,3) were observed. CH 4300 Å (0,0) and a very weak 3900 Å (0,0) band were detected in the acquired spectra. When increasing the C$_2$H$_2$ content in the C$_2$H$_2$: Ar mixture, intensities of Hα, Hβ lines and C$_2$ and CH band increase.

The thickness of the amorphous carbon films deposited on glass during 20 minutes varies with the C$_2$H$_2$ content in Ar (see Fig. 2). The thickness of the films can reach up to 50 µm at 2% of C$_2$H$_2$. At higher C$_2$H$_2$ contents the thickness of the films is decreasing down to 40 µm (at 2.5%) and 27 µm (at 3%). The highest deposition rate was achieved at 2% of the C$_2$H$_2$ content in the gas mixture.
There is a steady increase of the deposition rate from 0.1 µm/min (Ar) reaching the maximum of 2.5 µm/min at 2% C\textsubscript{2}H\textsubscript{2}. At higher C\textsubscript{2}H\textsubscript{2} contents the deposition rate starts to drop to 1.35 µm/min at 3% C\textsubscript{2}H\textsubscript{2}. A similar character of the deposition rate versus acetylene content was observed also by
other authors, however, at much lower deposition rates and at very high acetylene concentrations. The increase of thickness with increasing acetylene content evidences an increasing contribution of carbon, while reduction of the film thickness (at C$_2$H$_2 > 2\%$) can be explained by predominant etching of carbon by atomic hydrogen.

The amorphous carbon films deposited on the microscope glass slides exhibited very good adhesion ($LC3$ not reached) for several samples. The adhesion test results are shown in Fig. 3.

It was observed that the films deposited at 0\%, 1.5\%, 2.0\%, 2.5\% and 3.0\% of C$_2$H$_2$ contents in the gas mixture with Ar showed natural delamination right after the deposition. The lowest value for the first critical load ($LC1 = 1.43 \pm 0.06$ N) was observed for the sample deposited at 1\% of C$_2$H$_2$ (at a total flow of 1500 sccm), while the highest critical load ($LC1 = 2.32 \pm 0.10$ N) was observed at 0.25\% of C$_2$H$_2$. The lowest second critical load ($LC2 = 1.91 \pm 0.09$ N) was observed for the 1\% C$_2$H$_2$ and the highest critical load ($LC2 = 16.95 \pm 0.75$ N) was observed at 0.5\% of C$_2$H$_2$. This correlates with the visually observable areas of delamination for the samples. The lowest measured third critical load ($LC3 = 2.04 \pm 0.09$ N) was observed at 1\% of C$_2$H$_2$. The $LC3$ level was not reached even at 51 \pm 0.05 N pressure force for the samples deposited at 0.25\% and 0.5\% - these samples show a very good adhesion of the coating to the glass surface.

The adhesion tests show that low contents of C$_2$H$_2$ lead to improved adhesion of the amorphous carbon films at the conditions described in Table I. The low adhesion is observed for films deposited without acetylene (0\% of C$_2$H$_2$, the film thickness is 1.5 \µm) as well as at C$_2$H$_2$ contents larger than 1.5\% (film thicknesses are above 25 \µm). The optimum contents of acetylene in Ar are between 0.25\% and 0.5\%. From the optical observation the sample deposited at 1\% C$_2$H$_2$ appears more brittle where flacking/chipping off can be observed quite early during the scratch test.

The mixture ration C$_2$H$_2$/Ar can be used to control both the deposition rate and the film adhesion. The highest deposition rate doesn’t yield well adherent amorphous carbon films. Films deposited at deposition rates higher than 0.8 \µm/min were self-delaminating. The films were adhesive up to 16 \µm of thickness. The delamination can partly be caused by high film thickness. Evaluation of adhesion for the set of coatings deposited at varied deposition rates but having the identical thicknesses is planned for future experiments so that the effect of thickness can be eliminated.

It can be observed that at purely PVD regime (0\% C$_2$H$_2$ content), the film thickness is low (1.5 \µm) while in the hybrid (PVD/PE-CVD) deposition the thickness can be as high as 50 \µm. Most of the deposited material is evidently supplied from the C$_2$H$_2$ PE-CVD process. However, using

FIG. 3. Comparison of the adhesion scratch test characteristics at different C$_2$H$_2$ contents.
the graphite hollow cathode plates as a target for the PVD process guarantees that no unintentional doping appears in the carbon coatings.

IV. CONCLUSION

It was proved that it is possible to deposit very thick amorphous carbon coatings directly (without an interlayer) on glass by the Magnets-in-Motion (M-M) rf linear graphite hollow cathode in a hybrid mode at moderate pressures around 40 Pa. Well-adhered films were deposited with majority of carbon being delivered from the PE-CVD part of the process. The growth of adhesive thick films is promoted at low contents of C$_2$H$_2$ (from 0.25% to 0.5%) in the C$_2$H$_2$ + Ar gas mixture.

The C$_2$H$_2$ content in Ar controls both the adhesion and the deposition rate. The maximum deposition rate was reached at 2% C$_2$H$_2$ content in Ar, however, a very high deposition rate (above 0.8 µ/min) does not yield well adhered carbon films.

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