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Abstract. Hard diamond-like carbon (DLC) films were prepared on organic photoconductor (OPC) and PMMA (polymethyl methacrylate) samples by electron cyclotron resonance (ECR) CH_4–Ar plasma deposition with low substrate bias. The films exhibited a specific electrical resistivity above 1×10^{14} Ω cm and very high transmittance for the visible spectrum of 370–800 nm. The hardness of the OPC samples was increased at least fourfold after deposition of DLC films. The acceptance voltage, photodischarge rate and dark decay rate of the DLC-coated OPC samples were all improved, and reached optimal values for rf biases around −90 V. The results indicated that the deposition of hard DLC films on OPC is a very promising technique to lengthen the working lifetimes of the OPC materials.

1. Introduction

Hard diamond-like carbon (DLC) films have been receiving considerable attention due to their unique properties resembling those of diamond. Their extreme hardness, chemical inertness, optical transparency and low electrical conductivity have given DLC films strong potential for high-technological applications, such as transparent optical coatings or protective wear-resistant coatings [1–3]. In recent years, organic materials have been increasingly employed in printing instruments as photoreceptors and today represent the major materials technology [4]. However, compared with either amorphous selenium (Se) or silicon (Si), organic photoconductors (OPCs) are relatively soft and can easily be deformed [5]. Mechanical wear and tear abrasion, resulting from the friction between the drum and the cleaning brush or the paper inside the printer, is often believed to be a major limitation for prolonged normal operation of organic xerographic photoconductors [6]. A possible way reported to lengthen the operating lifetime of OPCs was to fabricate a high-hardness and low-friction coating on the OPC surface [7]. In addition, the protective film must be transparent in the visible spectrum, possess high electrical resistivity and should essentially not cause a deterioration of the electrophotographic properties of the OPC. Concerning all these requirements, DLC films seem to be a suitable candidate for the surface protection of OPCs as DLC films are hard, wear resistant materials with low coefficient of friction, high transparency and good insulating properties [1, 3, 8]. However, investigations on the electrophotographic properties of DLC film covered on organic photoconductors have so far only rarely been reported.

In this study, electron cyclotron resonance (ECR) CH_4–Ar plasma deposition was applied to prepare DLC films on rf-biased OPC and PMMA (polymethyl methacrylate) samples at temperature close to ambient. DLC films deposited on PMMA were used to carry out the optical investigations. To obtain hard, transparent DLC films with the optimum electrophotographic properties, the effects of the negative rf bias on the properties and the electrophotographic behaviour of DLC-coated OPC samples were systemically examined.

2. Experimental procedure

A commercial organic photoconductor (OPC) coated on an aluminum cylinder produced for a common model of laser printer was used as OPC samples in this study. DLC films were deposited onto OPC and PMMA substrates by using a microwave chemical vapour deposition apparatus assisted by ECR plasma [9]. Prior to film growth the substrates were subjected to a 15 min Ar^+ sputter cleaning with a rf bias of -100 V. The reactant stream was a mixture of pure CH_4 and pure Ar used in different flow ratios of CH_4 to Ar (or F_{CH_4}/F_{Ar}). The reactant pressure was maintained at less than 1.5×10^{-3} Torr. In order to prevent a rise of the substrate temperature above $100\,^\circ$C, the microwave power was fixed to 180 W and the negative rf bias was limited to -170 V. DLC films used for optical and electrophotographic investigation were all prepared at a thickness of about 150 nm.

The performance of an organic photoconductor was evaluated by the acceptance voltage, dark decay rate, photodischarge rate (the initial slope of the photodischarge) and residual potential [10]. All these electrophotographic properties were derived from the photodischarge curve (PIDC) which was measured for a layer sequence of an DLC/OPC/Al sample by using a computer-controlled tester [11].

The surface morphology of DLC films was observed by scanning electron microscopy (SEM). The film thickness was measured by a Tencor Instrumenta Alpha-Step® 500 Surface Profiler. A Matsuzawa MXT-α7 digital microhardness tester was employed to determine the film hardness on the Vickers scale with a load kept at 10 g. For the measurement of electrical resistivity, PMMA samples were firstly deposited a 30–40 nm thick Au film, and then followed by the deposition of DLC films. A Hewlett–Packard HP-4339A high resistance meter with HP-16117B clamping apparatus was used to measure the electrical resistivity of DLC films. The optical transmittance of DLC films on PMMA was measured by a UV/VIS spectrometer (Perkin Elmer Lambda 2S), and the transparency of the DLC films evaluated in the visible wavelength range between 370 and 800 nm.

3. Results and discussion

The prepared DLC films were visually very smooth and flat. No grain features could be observed under the SEM. For a negative rf bias of about $-(65–170)$ V, DLC films could be synthesized on OPC and PMMA samples by ECR CH_4–Ar plasma deposition with a rate higher than 0.05 nm s^{-1}.

The chemical binding structure, hardness and electrical resistivity of DLC films deposited on Si(111) wafers, as a function of both rf bias voltage and F_{CH_4}/F_{Ar}, have been separately studied and will be reported elsewhere [9]. The optimum deposition conditions, at which DLC films possessed sp^3-banded structure and reached a maximum hardness of above 3000 kgf mm^{-2}, were found at a microwave power of 180 W, $F_{CH_4}/F_{Ar} = 0.075$–0.086 and an rf bias of $-(80–100)$ V. However, the experimental results indicated that the structure

and the properties of so-formed DLC films are sensitive to the variation of the negative bias voltage [9].

Figure 1 shows the optical transmission spectra of DLC films deposited on PMMA substrates at different negative rf biases. It is apparent that DLC films prepared at rf biases of $-(80–100)$ V exhibit quite high optical transmittance in the whole visible wavelength range of 370–800 nm. The calculated optical band gaps based on the transmission ranges in figure 1 were between 2.2 and 2.7 eV. It was found that DLC films deposited on PMMA samples up to a thickness of 200 nm still exhibited a very good optical transmittance. It is, therefore, expected that the influence of DLC films on the photogeneration magnitude in the OPC will be negligible.
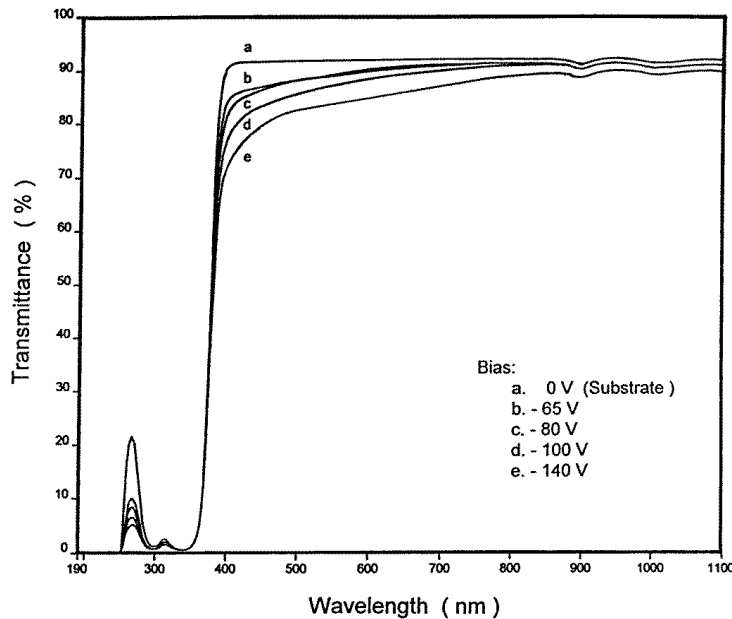

Figure 1. The spectral transmittance of DLC films prepared at different rf biasing.

The electrical resistivity and hardness of DLC films formed under different bias voltages were systematically measured for film thickness of above 200 nm. DLC films formed with negative biases of $-(65–170)$ V exhibited high specific resistivities above 1.0×10^{14} Ω cm, and reached maximum values of $(2.6–3.1) \times 10^{16}$ Ω cm when films formed at a bias of $-(80–100)$ V. The method used to calculate the film hardness in this study is the same as that in [10]. It was found that the microhardness of DLC films formed on PMMA and OPC at rf biases of $-(80–100)$ V was in a range of 52.5–74 kgf mm^{-2}. As compared with the hardness of OPC (12 kgf mm^{-2}) and PMMA (22.2 kgf mm^{-2}), DLC films remarkably increased the hardness to at least four and one times higher than those of bare OPC and PMMA, respectively. However, the hardness is much lower than that of DLC films deposited on Si(111) [9]. It may be assumed that the hardness of DLC films on OPC or PMMA is underestimated as the thickness of carbon films is too thin to be measured accurately.

The variation of the acceptance voltage of the DLC/OPC/Al samples with negative rf biasing is shown in figure 2. It is found that the acceptance voltage increases from 500 to
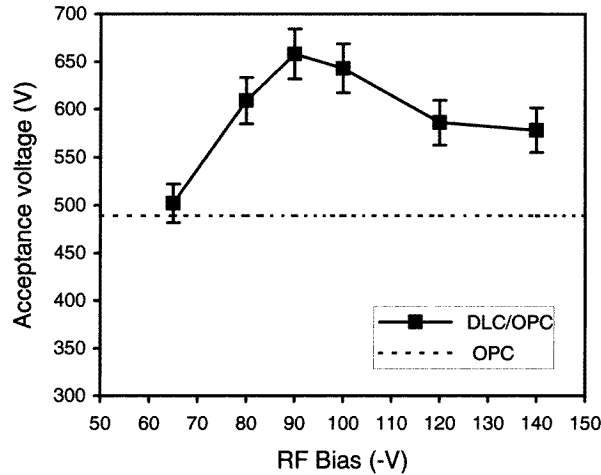
Figure 2. The acceptance voltage of the DLC/OPC/Al samples as a function of negative rf biasing used in the DLC film preparation.

a maximum of 650 V after the deposition of DLC films with an optimum rf bias voltage of -90 V.

Theoretically, when a homogeneous charge distribution resides at the surface, the surface potential is related to the charge density by the geometrical capacitance as [4]:

$$V = Q_s/C \tag{1}$$

where Q_s is the surface charge density, and C the capacitance. When a high electrical resistive DLC film is deposited on the OPC surface, the total capacitance C is the sum of the capacitance of the OPC and the capacitance of the DLC film connected in series:

$$1/C = 1/C_{OPC} + 1/C_{DLC} \tag{2}$$

or

$$C = (C_{OPC} \times C_{DLC})/(C_{OPC} + C_{DLC}) < C_{OPC}. \tag{3}$$

Thus, the acceptance voltage of DLC-coated OPC is larger than that of the original OPC for the same surface charge density, as shown in figure 2. The variation of the acceptance voltage of DLC films formed at various rf biases is due to the variation in light intensity reaching the charge generation layer (CGL) caused by optical interference [11].

Figure 3 is a graph of the dependence of the dark decay rate of DLC/OPC/Al samples on rf bias voltages. The measuring time was 2 s. The results illustrate that the dark decay rate is smaller than that of the unprotected sample when DLC films were prepared with rf bias between -80 and -140 V. The DLC films with high electrical resistivity can inhibit the surface charge injection [5], responsible for dark discharge, and thus lead to the observed decrease in the dark decay rate.

The variation of the photodischarge rate of the DLC/OPC/Al samples as a function of rf bias voltage is shown in figure 4. It is found that the photodischarge rate increases after deposition of DLC films, and reaches a maximum of 9700 V s^{-1} for the films synthesized also at -90 V rf biasing.

The initial discharge rate of the photodischarge curve is
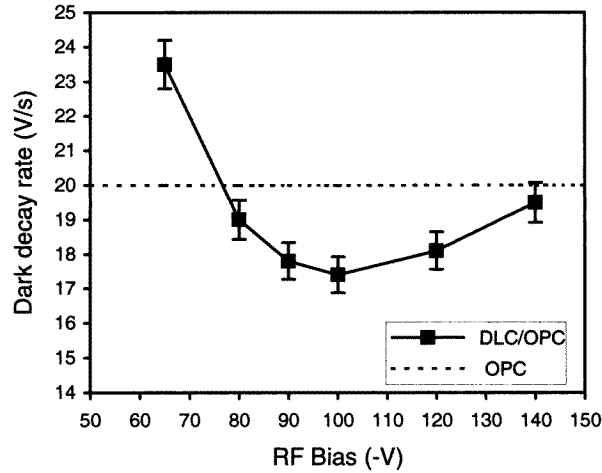
$$(dV/dt)|_{t=0} = \eta F/C \tag{4}$$

Figure 3. The dark decay rate of the DLC/OPC/Al samples as a function of the negative rf biases used in the DLC film preparation (measuring time: 2 s).
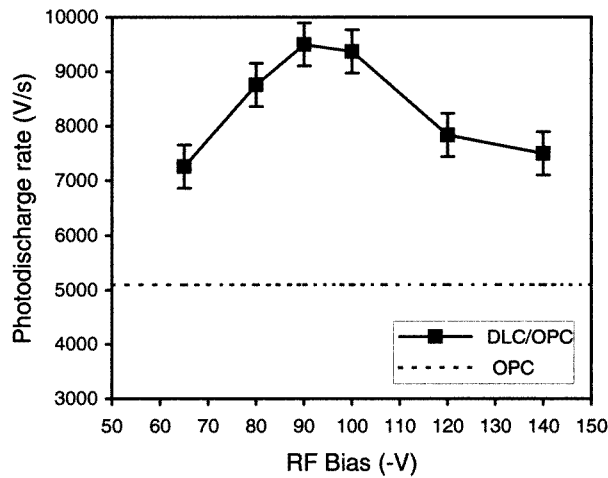

Figure 4. The photodischarge rate of the DLC/OPC/Al samples as a function of rf biasing.

where η is the efficiency of carrier generation (electric field dependent), F is the number of photons absorbed per unit time and unit area, C is the capacitance per unit area and e is the elementary charge. Thus, according to the equations (1) and (3), a decrease in the capacitance of the DLC-coated samples would cause an increase in the initial photodischarge rate, as shown in figure 4. Similar to the changes of acceptance voltages in figure 2 with respect to the negative rf bias, the variation of the photodischarge rate with rf biasing is also due to the variation of the F in the CGL caused by optical interference.

Figure 5 shows the variation of the residual potential of the DLC/OPC/Al samples with rf biasing. The residual potential exhibits small fluctuations but is very close to the residual potential of the unprotected OPC. Previously, an rf reactive sputtered AlN film was reported as a possible new protective coating for OPCs, but the residual potential
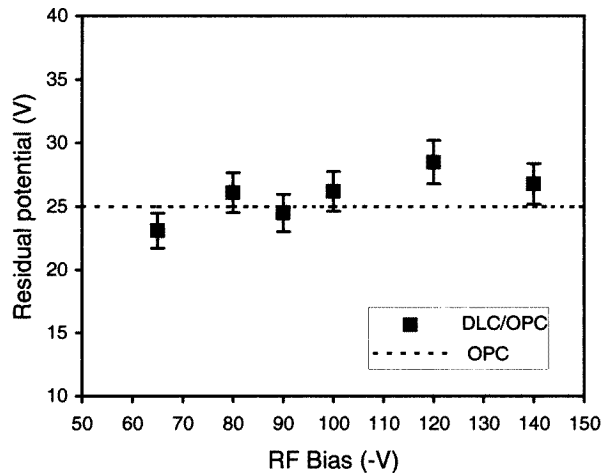
Figure 5. The residual potential of the DLC/OPC/Al samples as a function of rf biasing.

usually increased while the surface hardness was not increased very much [7]. This suggests that DLC films coated on OPCs seem to improve the electrophotographic properties more than AlN coating does, and may therefore be a more suitable protective coating on OPCs.

A good photoconductor for use in xerography should have a low dark decay rate and a high photodischarge rate. A high acceptance voltage and a low residual potential are also desirable to make a large contrast potential for good image development. The previous work indicated that DLC protective films can be successfully deposited onto OPCs by ECR CH_4–Ar plasma processing [10]. However, the properties of DLC films are strongly influenced by an ion bombardment energy [1, 3, 12]. When DLC films were prepared on negative self-biased substrates at a working pressure less than 1.5×10^{-3} Torr, according to the analyses of J Robertson, the bombarding ion energy (E_i) in ECR plasma was nearly equal to the absolute bias value ($|V_b|$) times the electron charge (e), i.e. $E_i \approx e|V_b|$ [12]. DLC films synthesized at an rf bias of $-(80$–$100)$ V were found to exhibit the maximum values in hardness, resistivity and optical gap energy [9]. It was argued that the $-(80$–$100)$ V rf bias would probably be the optimum energy window for ion impingement in ECR CH_4–Ar plasma processing, which promoted the growth of DLC films on low temperature substrates with a high fraction of sp^3 hybridized bonds. Accordingly, the present investigation has focused on the effect of negative rf bias on the electrophotograhic properties of DLC films. The study clearly indicates that DLC films deposited on OPC and PMMA at a bias of $-(80$–$100)$ V also exhibit extreme electrical resistivity and excellent optical transmittancy. Especially, the high optical transmittancy promises that the CGL receives the maximum light intensity at the same surface charge density, while the extreme electrical resistivity enhances the prevention of surface charge injection. All these unique characteristics lead to an optimal improvement of the electrophotographic properties of DLC-coated OPC samples by increasing the acceptance voltage and the photodischarge rate, and reducing at the same time the dark decay rate. In addition, deposition of DLC films strikingly increases the hardness of the OPC surface at least by a factor of four. It can be concluded that the deposition of hard DLC films on OPCs at an rf bias of around -90 V would also greatly extend the lifetime of OPCs in operation.

4. Conclusions

DLC films were successfully deposited onto OPCs and PMMA by an ECR CH_4–Ar plasma process at rf biases of $-(65$–$140)$ V; these films showed high transmittance in the whole visible wavelength between 370 and 800 nm. DLC films prepared at the optimum rf bias of $-(80$–$100)$ V remarkably increase the hardness of the OPC samples at least fourfold, and also show a high specific electrical resistivity of $(2.6$–$3.1)\times10^{16}$ Ω cm. Electrophotographic studies indicated that DLC-coated OPC samples exhibited an increase in both acceptance voltage and photodischarge rate, and a decrease in the dark decay rate; the optimum situations were reached when the rf bias was kept around -90 V during the film formation. In addition, the residual potential was almost the same as that of an unprotected OPC sample. Therefore, the preparation of DLC film by using ECR CH_4–Ar plasma is very promising to improve both the electrophotographic properties and the hardness of the OPC materials.

Acknowledgments

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