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DEPOSITION OF DIAMOND-LIKE CARBON FILMS[1]

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Amorpohous diamond-like carbon layers have been deposited using an r.f. discharge excited in CH_4, C_2H_2, C_6H_6 as working gases. Carbon films grown in this way have some remarkable properties: they are insulating (10^{12} Ωcm), have a high dielectric strength (10^6 V/cm) and extreme hardness (4000 HV).

НАНЕСЕНИЕ АЛМАЗООБРАЗНЫХ УГЛЕРОДНЫХ ТОНКИХ ПЛЕНОК

При помощи высокочастотного разряда, возбужденного в рабочих газах CH_4, C_2H_2 и C_6H_6, проведено нанесение аморфных алмазообразных углеродных пленок. Углеродные пленки, полученные таким образом, имеют некоторые очень хорошие свойства. Они обладают высокими изоляционными свойствами (10^{12} Ωм.см), большой электрической прочностью (10^6 В.см$^{-1}$) и исключительной твердостью (4000 HV).

I. INTRODUCTION

Hard, electrical insulating films with a low friction coefficient have numerous potential applications. Diamond-like (i-C) films can be made by r.f. plasma decomposition from hydrocarbon gases [1—5], by low energy carbon ion beam deposition, by ion plating and by dual beam techniques [6—9].

Extreme hardness, chemical inertness, high resistivity, high wear resistance and dry lubricating properties make these i-C films suitable for use as a dielectric or protective coating and for bearing where oils and greases cannot be employed [10—13].

The present paper describes the deposition of i-C films by r.f. plasma deposition involving self-bias voltage in a barrel discharge vessel. The optical, electrical and mechanical properties of the films prepared are also presented.

II. EXPERIMENTAL

The process chamber used for depositing the i-C films is shown in Fig. 1. A discharge tube of fused silica (internal diam. 42 mm, length 920 mm) was placed in the furnace. Both ends of the silica tube were provided with stainless flanges. The exit flange was connected with a vacuum pump. The second (inlet) flange was provided by fixing bolts and a removable cover with a connector of an r.f. generator and a sample holder. Inlet gas flows were controlled by hand with needle valves and the pressure was controlled by throttling the vacuum valve and measured with a MKS Baratron capacitance manometer and a Pirani vacuum gauge.

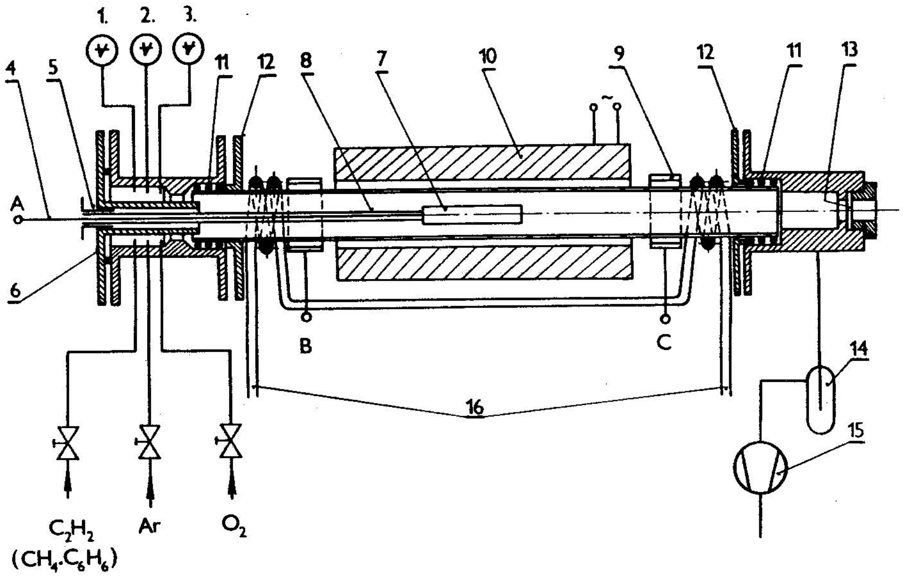

Fig. 1. Experimental arrangement of the furnace reactor tube for r.f. self-bias deposition of i-C films. 1, 2 — MKS Baratron vacuum gauges, 3 — Pirani vacuum gauge, 4 — r.f. supply line, 5 — ceramic insulator, 6 — removable cover of the inlet flange, 7, 8 — substrate holder with support, 9 — external electrodes, 10 — furnace with resistance heating, 11 — rubber gasket rings, 12 — sealing of flanges to quartz tube, 13 — quartz observing window, 14 — cool trap, 15 — rotary oil pump, 16 — water cooling.

Methane, acetylene and benzene diluted with argon were used as working gases. The 1.5 MHz r.f. power input (70 W max.) was fed to the substrate holder and to two external electrodes on the silica discharge tube. The sample holder is capacitively coupled to an r.f.-bias sputtering generator. Fig. 2 shows a schematic diagram of the r.f. power circuitry used in our investigations. In order to clean the

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substrates argon of 99.9 % purity is let in so that the pressure is increased to about 12—80 Pa. The Ar plasma causes a pre-sputtering of the substrates. Next, the reacting gas (CH_4, C_2H_2, C_6H_6) is added to Ar, and the final partial pressures are adjusted to $p_{Ar} = 0$—70 Pa, $p_{r.g.} = 10$—40 Pa.

The light emitted from the capacitively coupled discharge plasma was detected by a monochromator with photomultiplier. The refraction index and i-C films thicknesses were measured by the ellipsometric method. The electrical resistivity and breakdown voltage were measured on the sandwich Al-i-C film-Al system.

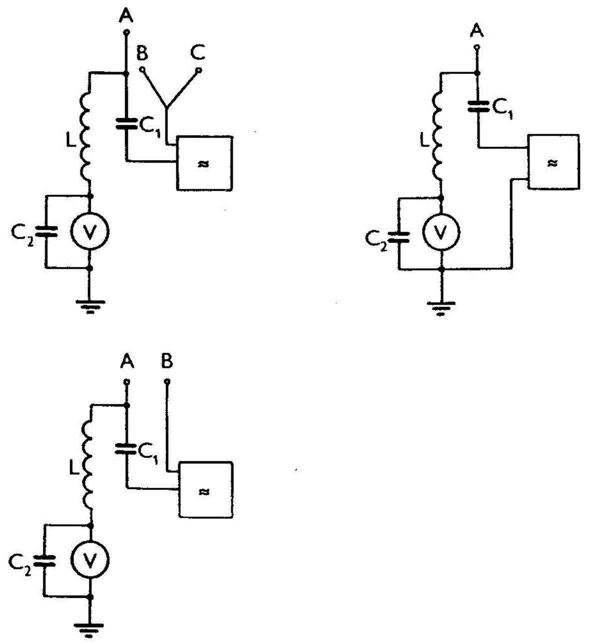

Fig. 2. Radiofrequency power circuitry for variable self-bias operation of r.f. generator. Connections A, B, C correspond to A, B, C in Fig. 1.

III. RESULTS

The i-C films were deposited on different substrates (Si, glass, steel, cemented carbides) by cracking CH_4, C_2H_2 and C_6H_6 under widely different conditions. By varying the bias voltage, the total and partial pressures of reactants i-C layers with quite different properties can be produced, ranging from soft polymeric insulating transparent layers through hard diamond-like insulating less transparent layers to hard graphite-like weakly conducting absorbing layers.

Carbon films prepared at a low bias voltage (<150 V) and low temperature (<100 °C) were transparent, soft with an index of refraction ranging from 1.5 to 1.7. Films prepared at bias voltage (150—400) v and low temperatures were hard (diamond-like) and yelow-brown. At higher temperatures (>300 °C) and higher bias voltages (>500 V) graphitization of deposited layers was observed.

The capacity and electrical resistivity of the sandwich systems (Al-i-C film-Al) are independent of humidity and this fact may be attributed to the pinhole-free layers. X-ray beam diffraction analyses show that the deposited i-C Films consist of amorphous phases. Spectroscopic analyses of optical emission during the deposition of i-C films were used to obtain a better understanding of plasma chemistry involved in these systems. Some representative results are in Tab. 1.

Table 1

		Organic compound C_6H_6	C_2H_2	CH_4
$p_{org.\,comp.}$	[Pa]	15	10	15
p_{Ar}	[Pa]	—	20	30
p_{total}	[Pa]	15	30	45
U_{bias}	[V]	310	260—300	240—260
Furnace temperature	[°C]	25	25	25
Deposit time	[min.]	1	15	4
Thickness	[nm]	125	360	100
Flow rate	[sccm]	4.2	14.3	31.0
Resistivity	[Ωcm]	10^{12}		10^7
Hardness	[HV]	—	—	3600
Breakdown voltage	[V/cm]	5×10^6	—	—
Refraction index	2.1	2.16	2.0	
Absorption coeff.	[cm^{-1}]	3×10^4	8×10^4	—
Substrate	Si glass	Si glass	Si glass	
Characteristic spectra	H, O, C, C^+, CH, N_2	H, C, C_2, CH_2, $C_4H_2^+$	H, O, O^+, C, C^+, CH, N_2	

IV. CONCLUSION

We have prepared diamond-like carbon films by r.f. plasma deposition using the non-conventional barrel system. The deposited i-C films are highly insulating and hard with a low friction coefficient. A major difficulty is the great intrinsic stress present in i-C layers, which makes it impossible to produce layers more than 1 μm thick on technologically interesting materials.

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