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THIN CARBON AND BN FILMS PREPARED BY RF PLASMA DEPOSITION[1])

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Hard amorphous carbon films were prepared by a combined technique involving rf bias sputtering with C electrodes and plasma decomposition of C_6H_6 vapours.

Insulating, hard BN films were prepared at a temperature below 500 °C by the rf glow discharage decomposition of a $B_2H_6 + Ar + NH_3 + N_2$ gas mixture.

I. INTRODUCTION

Hard "diamond like" amorphous carbon films and hard amorphous BN films have attracted considerable attention in recent years because of their potential utilization as protective and passivation coatings [1—3]. The majority of investigations have concentrated on films prepared from a plasma ionized hydrocarbon and organic boron species by employing dc or rf glow discharge and ion beam sputtering techniques [4—14]. In this paper are reported results obtained with the planar rf deposition system where the rf bias sputtering of the pure carbon target is combined with the rf plasma decomposition of C_6H_6. The structure, electrical and optical properties of the deposited films were investigated.

Stoichiometric boron nitride is highly insulating, chemically inert, hard and thermally stable [15—17]. A new class of boron nitride films was prepared at a temperature below 500 °C by the glow discharge decomposition of a $B_2H_6 + Ar + NH_3 + N_2$ gas mixture.

II. EXPERIMENT

Hard carbon films were deposited in an rf bias sputtering system consisting of two parallel-plate rf electrodes — Fig. 1. The upper electrode (10 cm diam.)

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was water cooled and the bottom electrode (16 cm diam.) was used as a substrate holder. The two electrodes were covered with pure carbon (99.999%) plates. The pumping system is a conventional diffusion pump — rotary mechanical pump system. Vapours from fluid C_6H_6 can leak into the system by means of a needle valve. The total pressure during plasma deposition was measured with a Pirani vacuum gauge and Baratron absolute pressure gauge. The bias voltages on the upper and lower electrodes could be varied independently by a system of variable capacitors in the matching network.

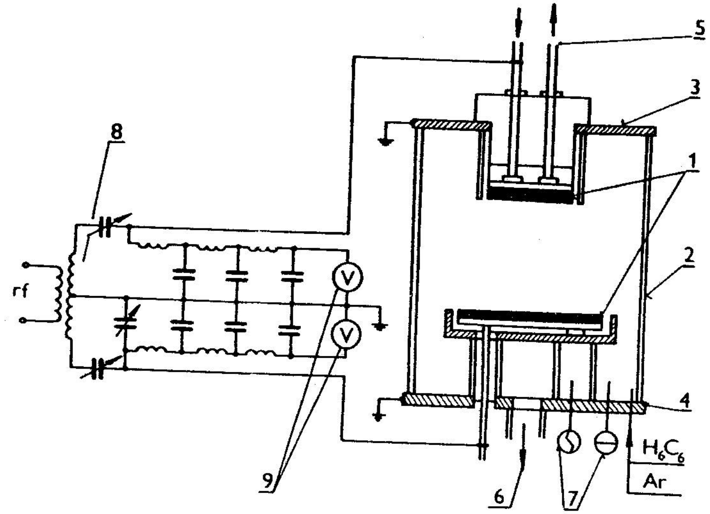

Fig. 1. Scheme of rf plasma reactor for producing hard carbon films from C_6H_6 vapours: 1 — upper and bottom carbon electrodes, 2 — glass vessel, 3 — upper steel cover, 4 — bottom steel cover, 5 — cooling water, 6 — to pump, 7 — vacuum gauges, 8 — rf matching network, 9 — DC voltmeters for self bias measurement.

For thin film deposition the system is first evacauted to a pressure of 10^{-3} pa then the Ar discharge is started in order to sputter clean the upper target electrode and partially the substrate protected with a shield. Subsequently, C_6H_6 vapours leak into the system; in the course of these investigations the parameters varied were the pressure (5—20 Pa), the upper electrode bias voltage — U_H (-200 to -800 V) and the substrate bias voltage — U_L (0 to -600 V). The rf power supplied in the reactor at the frequency of 27 MHz was < 1 kW. The substrates used for various studies include: Si, glass, cemented carbides. The BN film deposition equipment, as shown in Fig. 2 is similar to the conventional PE CVD barrel system (i.d. 45 mm), employing a reaction between B_2H_6 and NH_3

(resp. N_2). The deposition is carried out at low temperatures $\leqslant 500$ °C. The pressure of the reactants for film production was controlled by a system of needle valves and measured with MKS Baratron and Pirani vacuum gauges. The rf discharge was excited capacitively at the frequency of 1.5 MHz (P_{max} — 70 W) by supplying rf power through one external ring electrode and the substrate support. A mixture gas of 2% B_2H_6 diluted in Ar + NH_3 or N_2 was admitted into a horizontal quartz tube reactor.

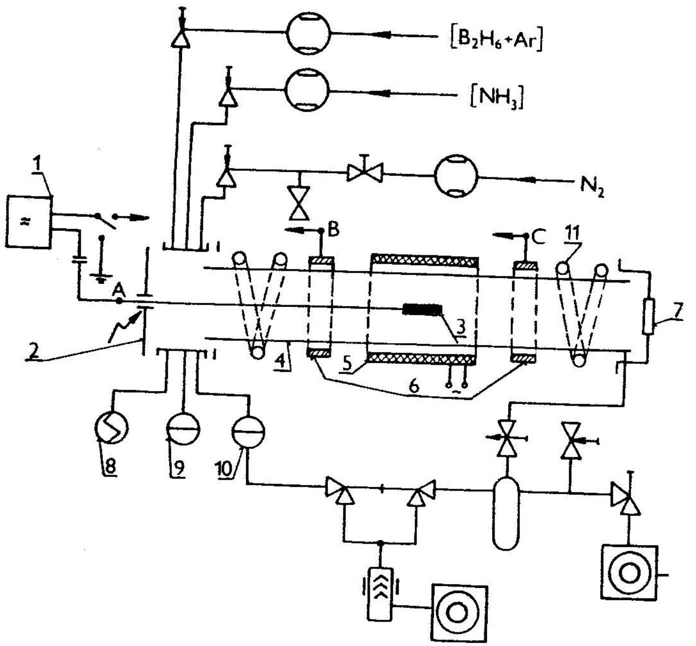

Fig. 2. Experimental arrangement of the reactor tube for deposition of hard BN films: 1 — rf generator, 2 — removable cover of the inflet flange, 3 — substrate holder, 4 — quartz tube, 5 — furnace with resistance heating, 6 — external electrodes, 7 — quartz window, 8, 9, 10 — Pirani and MKS Baratron vacuum gauges, 11 — water cooling, 12 — self bias voltage measurements.

The refraction index and film thicknesses were measured by the ellipsometric method. The electrical resistivity and breakdown voltage were measured on the sandwich Al — thin film — Al system. Film hardness was determined using a Vickers microhardness pyramid diamond indenter. Structural properties were studied using TEM and electron diffraction methods.

III. RESULTS AND DISCUSSION

In order to prepare hard carbon films of reproducible properties the various deposition parameters had to be analysed. The rf power can be tuned; however the net rf power coupled into the system is not uniquely correlated with the deposition process since there can be substantial power losses in the matching unit. The self bias voltages U_H, U_L and the total pressure are the significant parameters. The growth rate at various U_H, U_L and pressure is given in Figs. 3, 4. Refractive indices of some measured samples as functions of U_L, U_H and pressure are presented in Tab. 1. Refractive indices of C layers prepared on glass substrates are slightly lower than those deposited on silicon.

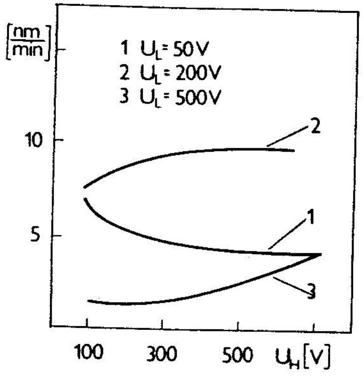

Fig. 3. Growth rate of carbon film vs U_H and U_L. C_6H_6 pressure = 5 Pa.

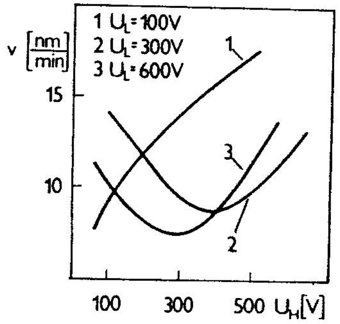

Fig. 4. Growth rate of carbon film vs U_H and U_L. C_6H_6 pressure = 8 Pa.

An important characteristic is the conduction process through the insulating C film. Therefore, MIM structures were prepared, where Al — C film and Al were succesively deposited on a glass substrate. Electrical conductivity of C films was determined from the leakage current at dc and ac (10^3 Hz) applied electric field. The conductivity depends on the U_H and U_L as can be seen in Fig. 5. The relative permitivity ε is about 3—5 and is also dependent on the U_H and U_L level used during deposition. The values seem to vary statistically but the dependence on the thickness of the C layer was also conspicuous — Tab. 1. Microhardness measurements were made using a lightly loaded Vickers diamond indenter. The films were significantly harder than silicon substrate (up to 4000 HV). Because Vickers hardness numbers are strong functions of load at light loads, these numbers have relative significance only and cannot be compared to values obtained at higher loads. Most of the diamond-like films examined in the present work were predominantly amorphous but the cristalline phases in most cases were sparsely distributed in a matrix that was amorphous. Scanning electron microscopy (SEM) revealed polycrystalline particles. The particles of several tenths of nanometers in size were observed by TEM (transmission electron microscopy) to obtain a distinctive diffraction pattern. Electron diffraction also shows presence of single-crystalline particles with diamond structure. Deposited carbon layers on Si exhibit compressive stress which is trongly dependent on the deposition parameters. Since the interaction between the carbon atom and the silicon of the substrate is thought to be strong, the

Table 1

n is the refractive index, k is the extinction coefficient, ε is the relative permittivity and ϱ is the specific resistivity.

P (C_6H_6) [Pa]	U_L [V]	U_H [V]	Substrate	t_{dep} [min]	d [nm]	n	k	ε	$\varrho = \varrho$ [cm]	(1 kHz) [cm]
5.5	100	250	Si	15	235	2.06	0.01			
5.5	100	300	glass	15	138	1.91	0.01			
5.0	200	300	Si	10	—	2.11	0.05			
5.5	100	100	Si	15	250	2.10	0.01			
7.0	100	400	glass	5	59	1.59	0.001			
7.0	200	400	Si	5	50	2.06	0.001			
8.0	300	500	Si	10	—	2.56	0.1			
5.5	150	400	Al (MIM)	5	40	—	—	3.5	4×10^{10}	2×10^{10}
4.5	300	400	Al (MIM)	10	110	—	—	3.8	5×10^{11}	4×10^{11}
5.5	100	150	Al (MIM)	5	20	—	—	5.1	3×10^{6}	2×10^{6}
5.5	100	350	Al (MIM)	10	100	—	—	4.7	4×10^{7}	3×10^{7}

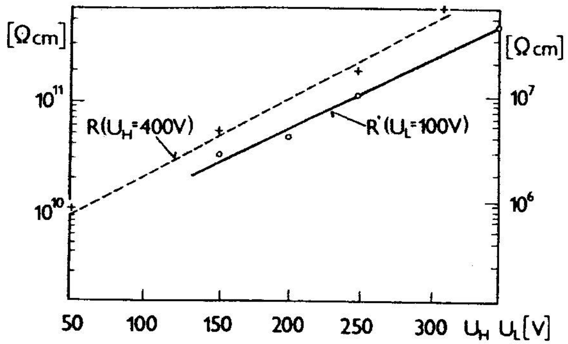

Fig. 5. Specific electrical resistivity as a function of self bias voltage U_H and U_L.

diamond probably nucleates in the gas phase or the nuclei are probably hydrocarbons which have weak interactions with the silicon surface before the degradation of the carabon-hydrogen bonds.

BN-films were deposited on silicon, glass and cemented carbides in the reactor described in Fig. 2. The properties of BN films produced in one deposition cycle varied from soft polymeric-like films, deposited in the inlet portion of the reactor through hard amorphous films growing in the central part of the rf discharge to white powder (hexagonal) BN) observed in the exit part of the discharge tube. Physical and chemical properties also depend on the rf power supplied to small powered substrate holder. The refractrion index varied from 1.6 to 2.6, the maximum of microhardness extrapolated for zero load was 5000 HV. Some typical deposition conditions of a selection of films prepared on Si (111) are given in Tab. 2.

Table 2

P (NH_3) [Pa]	P ($B_2H_6$2% + Ar) [Pa]	P (N_2) [Pa]	t [min]	T [°C]	d [nm]	n	Hardness [HV]
150	150	—	6	400	74	2.66	
120	120	—	5	500	91	2.54	
100	150	—	6	300	54	2.22	
10	90	—	5	300	36	1.63	
50	200	—	40	300	830		900
—	80	20	10	400	750		3000 1)
—	80	20	1	400	74	2.60	
—	80	20	10	400	850		5000 2)

1) power input 55 W.
2) power input 35 W.

IV. CONCLUSIONS

It has been shown that highly insulating, hard carabon films can be produced using C_6H_6 and pure carbon electrodes in a planar rf sputtering reactor. The films have excellent dielectric and optical properties and are highly resistant to wear, abrasion and chemical attack. Electrical properties of carbon films can be modified tahrough the self bias voltage U_H and U_L.

A method of BN films deposition was described using $B_2H_6 + Ar + NH_3(N_2)$ as starting materials. The film properties are very sensitive to the process parameters, particularly on the specific rf power input and to the position of the substrate in the discharge tube.

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ТОНКИЕ ПЛЕНКИ ИЗ УГЛЕРОДА И BN, ПРИГОТОВЛЕННЫЕ МЕТОДОМ ОСАЖДЕНИЯ ПРИ ВЫСОКОЧАСТОТНОМ ПЛАЗМЕННОМ РАСПЫЛЕНИИ

Твердые аморфные углеродные пленки приготовлены при помощи комбинированного метода, который позволил использовать высокочастотное плазменное распыление с углеродными электродами и плазменное разложение паров C_6H_6. Отдельно при температуре ниже 500 °Ц были приготовлены тонкие пленки из BN при помощи разложения смеси газов $B_2H_6 + Ar + NH_3 + N_2$ в высокочастотном тлеющем разряде.