

HYDROCARBON PLASMA POLYMER FILMS PREPARED BY RF SPUTTERING OF POLYETHYLENE

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Radio frequency sputtering of polymers have been applied for preparation of plasma polymer films namely fluorocarbon ones since the seventies of the last century [1-10]. The reason for these investigations was apparently to prepare good dielectric films, low friction coatings and optical applications [9]. In addition to fluorocarbons also polyimide [7] and polyethylene [8] were sputtered. Nevertheless information about films chemical structure dependence on sputtering conditions is not sufficient and need more investigations.

In this study we focus on RF magnetron sputtering of polyethylene (UHMW ET303250 Goodfellow, target thickness was 2.5 mm) using argon as a working gas. We used a parallel plate electrode system with an RF planar magnetron (80 mm in diameter, RF frequency – 13.56 MHz) facing up with the substrate placed 50 mm from the magnetron. The sputtering was performed at a pressure of Ar in ranging from 2 to 6 Pa, RF power 20-200 W and Ar flow rate 8 sccm.

AFM (Quesant Q-Scope 350), ESCA (Kratos-165), FTIR (Nicolet Impact 400) techniques were used for film characterisation. Examples of AFM observation of sputtered PE film are in Fig. 1(a-b). The deposition rate was measured by QCM (MT 01). The average deposition rates 0.04 nm/minW were obtained (Fig. 2) that is several times lower than in case of sputtering of PTFE [10]. FTIR spectra of polyethylene target and sputtered films are in Fig. 3. with possible absorption band assignment in Table 1. Four strong IR absorption peaks (bands A-C) inheriting to polyethylene were founded in DRIFT spectra of PE target (fig. 3(a)).

The films sputtered at powers lower than about 100 W have a complex chemical structure as usual for hydrocarbon plasma polymers (fig. 3(c-d)). There are new groups as compared to original polyethylene target (Table 1). Films contain oxygen at least at the surface as shown by ESCA – the ratio O/C is 0.5. The high-resolution ESCA spectra of C 1s peak (285.0 eV) show presence C=O (286.2 eV) and C-O-C (288.7 eV) groups on the surface. The reason may be oxygen incorporation during sputtering. In addition some oxidation may be caused when sputtered films are exposed to the open atmosphere.

Above 100 W melting of the PE target took place in the erosion zone. These films are co-sputtered/evaporated with increased surface roughness (Fig. 1(b)). They are, however, softer and more resemble according to FTIR original PE (Fig. 3(b)). It should be noted that when evaporation takes place the deposition rate is at least ten times higher in comparison with sputtering at low RF power.

The “evaporated” films are more polymer-like. Deconvolution of CH stretching absorption peak around 3000-2800 into five Voigt profiles corresponding to specific stretching vibrations (Fig. 4-5) shows the considerable weaker absorption due to the –CH₃ groups for these films. There is a clear contribution from $\nu_{as}CH_2$ in the IR spectra “evaporated” films that correspond to polymer-like materials [11]. The intensity of all the CH absorption groups in this case is ten times higher compared to films sputtered up to 100 W that is another characteristic of polymer-like material. The “evaporated” films consist of fragments of polyethylene chain with branching structure. The evidence of this suggestion is the absence in the FTIR spectra (fig. 3(b)) absorption band at 730 cm⁻¹ due to changing in skeletal stretching vibrations.

Two distinct modes of PE sputtering were found in current research. The lower power “classic” sputtering produces very complex hydrocarbon polymer films, while the higher power sputtering gives the coatings, which have more in common with traditional PE.

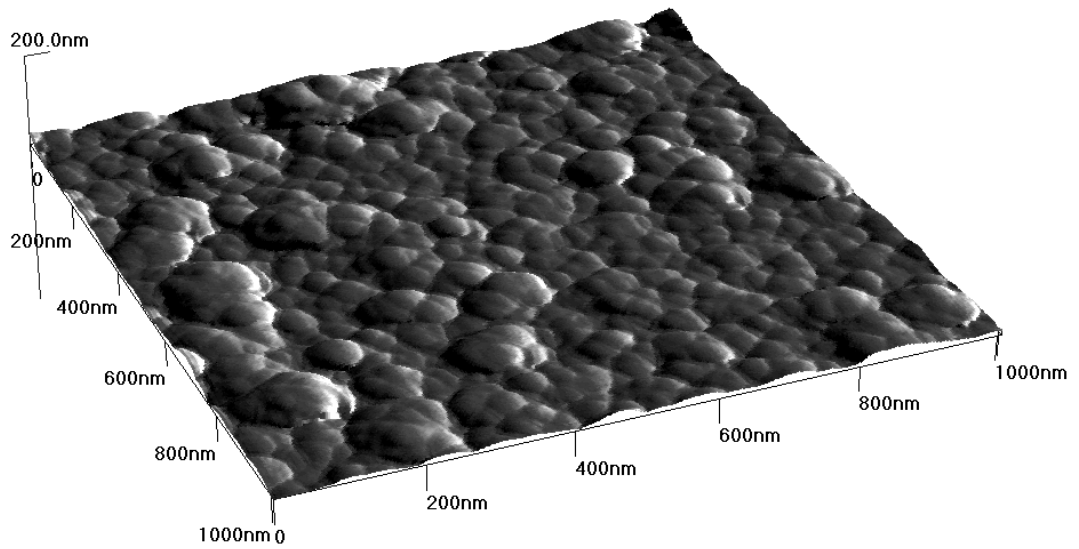


Fig. 1(a). Surface of sputtered polyethylene film without evaporation.
 Ar pressure 4 Pa, RF power 100 W, $U_{\text{bias}} = -526$ V, Ar flow rate 8 sccm/min, deposition time 60 min, film thickness 245 nm

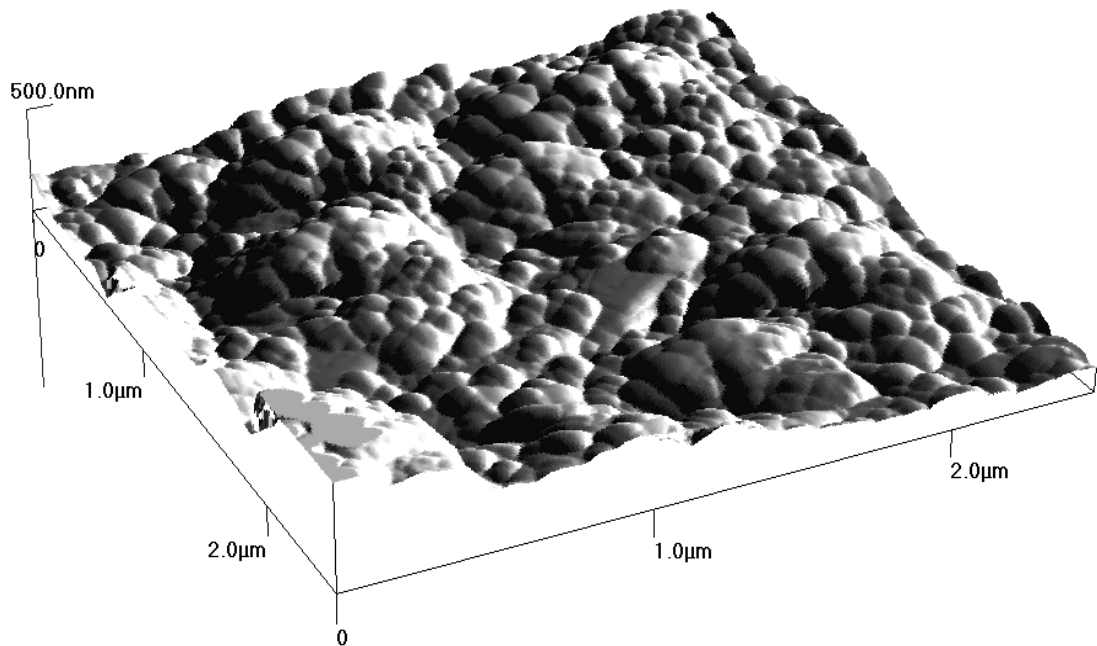


Fig. 1(b). Surface of sputtered polyethylene film when some evaporation took place.
 Ar pressure 4 Pa, RF power 200 W, $U_{\text{bias}} = -540$ V, Ar flow rate 8 sccm/min, deposition time 5 min, film thickness 600 nm

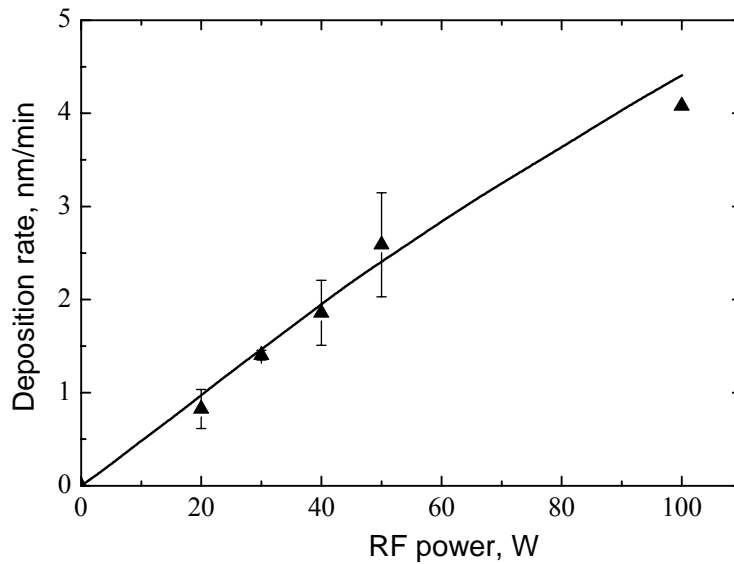


Fig. 2. Dependence of deposition rate of polyethylene on RF power at Ar pressure 4 Pa.

Table 1. Possible assignment of IR absorption bands

Band	ω, cm^{-1}	Vibration
Polyethylene		
A	2960	$\nu_{\text{as}}(\text{CH}_3)$
	2925	$\nu_{\text{as}}(\text{CH}_2)$
	2900	$\nu(\text{CH})$
	2875	$\nu_{\text{s}}(\text{CH}_3)$
	2855	$\nu_{\text{s}}(\text{CH}_2)$
B	1473, 1463	$\delta(\text{CH}_2)$, doublet
	1460	$\delta_{\text{as}}(\text{CH}_3)$
	C	1375
D	720, 731	$\gamma(\text{CH}_2)$, doublet
	Films	
1	3500-3200	$\nu(\text{OH})$, $\nu(\equiv\text{CH})$, $\nu_{\text{over}}(\text{C}=\text{O})$
2	2970-2850	As band A
3	2200	$\nu(-\text{C}\equiv\text{C}-)$, $\nu_{\text{as}}(>\text{C}=\text{O}=\text{O})$
	2130	$\nu(-\text{C}\equiv\text{CH})$
4	1680-1580	$\nu(\text{C}=\text{C})$, $\nu(-\text{C}=\text{O})$
5	1455	$\delta(\text{CH}_2)$, $\delta_{\text{as}}(\text{CH}_3)$
6	1375	$\delta_{\text{s}}(\text{CH}_3)$
7	1070-1030	$\nu(-\text{C}-\text{O}-\text{C}-)$, $\nu(-\text{C}-\text{O}-\text{H})$
8	700-500	$\gamma(\text{CH}_2)$, $\gamma(\text{CH})$, $\delta(\equiv\text{CH})$, $\delta(\text{OCO})$

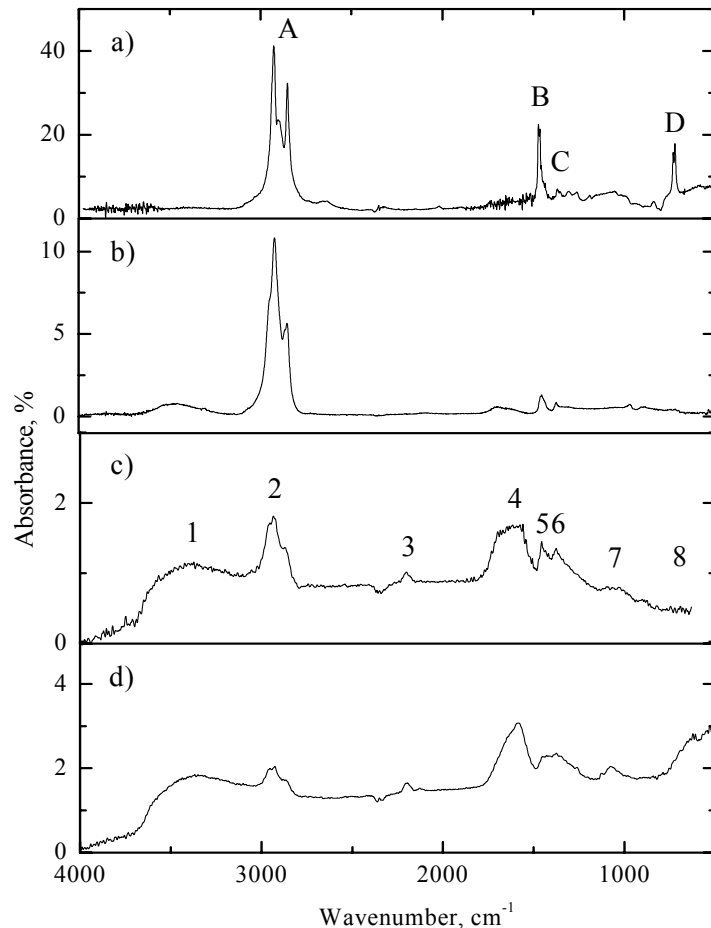


Fig. 3. FTIR spectra of polyethylene target (a) and polyethylene films (b-d): original polyethylene, sputtered at 200 W with some evaporation, sputtered at 100 W, sputtered at 50 W.

Absorption bands in the region of CH groups stretching vibration of FTIR spectrum and their possible curve fitting.

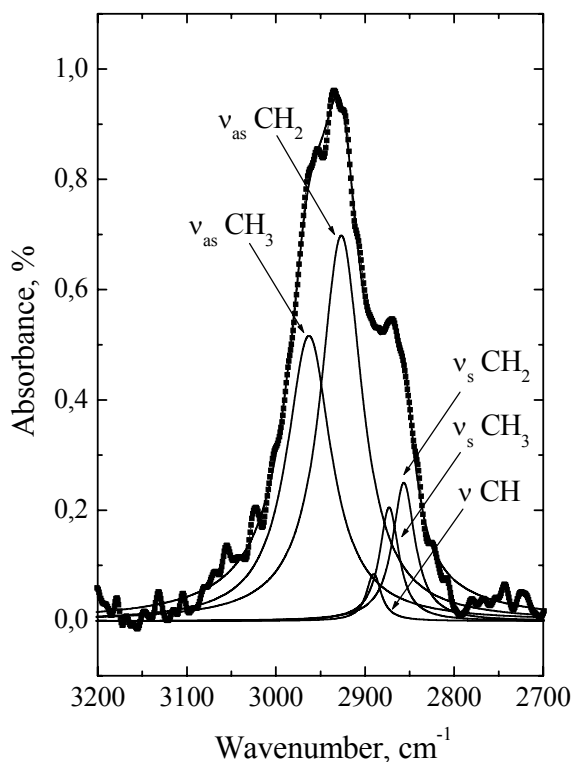


Fig. 4. Film sputtered at 100 W

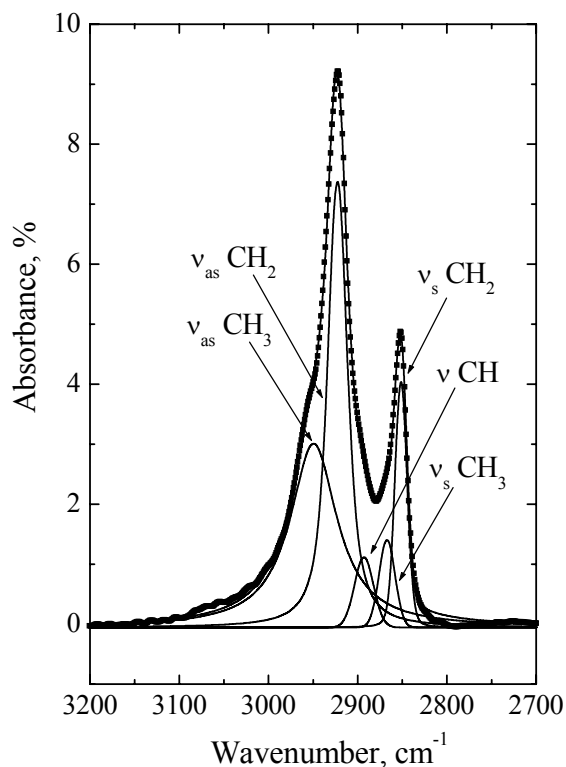


Fig. 5. Film co-sputtered/evaporated at 200W

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