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Polymerization of Ferrocene in an Electrodeless High-Frequency Discharge Helium Plasma:

II.[1] Structure and Crystallization Dynamics of Plasmochemically Polymerized Films

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Abstract—The main frequencies in the IR spectra of ferrocene and plasmochemically polymerized ferrocene films obtained in the plasma of an electrodeless high-frequency discharge in mixtures of helium and ferrocene are the same. The appearance in the IR spectra of the films of weak bands is associated with partial decomposition of ferrocene molecules in the high-frequency discharge plasma.

Earlier we showed [1] that the polymerization of ferrocene in an electrodeless high-frequency discharge helium plasma involves partial decomposition of ferrocene molecules in the gas phase and formation of electronically excited iron atoms. The plasmochemical polymerization gives rise to plasma-polymerized ferrocene films which have a constant composition throughout the sample thickness. The X-ray electron spectra of the films showed that iron atoms in them are not bound with carbon into iron carbides, and the films exhibit pronounced getter properties with respect to oxygen, as a result of which iron in the sample matrix after atomization of the surface layer of the film is rapidly oxidized to form iron oxides. It was also shown that the element composition of the plasmochemically polymerized ferrocene film only slightly differs from the composition of the starting ferrocene molecule. The C/Fe ratio in ferrocene ($C_{10}H_{10}Fe$) is 10. The element composition of the film taken from walls of the plasmochemical reactor corresponded to the formula $C_{8.8}H_{9.9}FeO_{1.5}$ (C/Fe ratio 8.8).

The resulting data allowed a mechanism of plasmochemical polymerization of ferrocene to be proposed, involving formation and subsequent reactions of the molecular ion $[FeCp_2]^+$ or the fragment ion $[FeCp]^+$ with plasma electrons or neutral ferrocene molecules. The reaction with plasma electrons finally yields electronically excited iron atoms Fe^*. The reactions of the molecular or fragment ions with neutral ferrocene molecules may give rise to more complex iron-containing ions like the multiple-deck sandwich ions $[CpFeCpFeCpFeCp]^+$ [2] close in composition to the starting ferrocene molecule $FeCp_2$. Recombination of such simple or more complex iron-containing ions in the gas phase or on the support surface with electrons results in deposition of polymeric films close in element composition to the starting ferrocene.

In the present work we compared the IR spectra of the plasmochemically polymerized ferrocene films and the starting ferrocene molecule and also studied the crystallization dynamics of and structural changes in the films under electron beam. Figure 1 depicts the IR spectra of ferrocene and its plasmochemically polymerized film. As seen from the figure, the ferrocene bands are preserved in the spectrum of the film. However, it should be noted that the spectrum of the polymeric film indicates a sharp fall of transmission compared with ferrocene. A possible reason for this phenomenon is the presence of ultradisperse iron particles in the film. The IR spectra of ferrocene and plasmochemically polymerized ferrocene films contain absorption bands assignable to Cp_2Fe skeleton vibrations (477 and 490 cm^{-1}) and Cp ring vibrations (812, 1000, 1100, 1400, and 3100 cm^{-1}) [3, 4]. It should be noted that the principal absorption bands of plasmochemically polymerized ferrocene films strictly coincide with those of ferrocene. Thus, the IR spectra of the films provide indirect evidence for the mechanism of ferrocene polymerization in an electrodeless high-frequency helium plasma, proposed in [1]. As judged from the IR spectra and elemental analyses, no profound decomposition of ferrocene molecules

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[*] For communication I, see [1].

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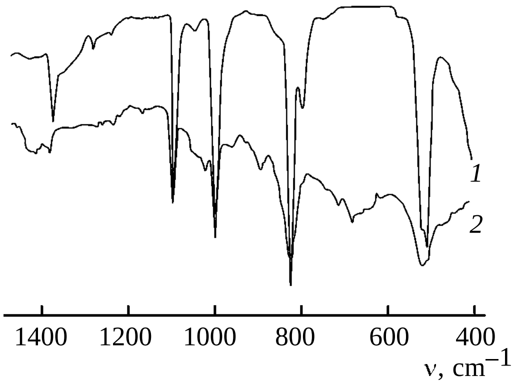


Fig. 1. IR spectra of (*1*) ferrocene and (*2*) plasmochemically polymerized ferrocene film.

occur. We deal here with a nonequilibrium weakly ionized plasma ($n_0 \sim 2\times10^{16}$ cm^{-3}, $n_e \sim 1.6\times10^{11}$ cm^{-3}, plasma ionization degree $\alpha = n_e/n_0 \sim 10^{-5}$, mean plasma electron energy ca. 6–7 eV [5]). Consequently, major processes involving plasma electrons most likely result in formation of the molecular ion of ferocene [scheme (1)] and its subsequent reactions with plasma electrons, yielding electronically excited products [schemes (2) and (3)] or with neutral ferrocene molecules to give more complex molecular ions [scheme (4)].

$$\mathrm{FeCp_2} + \bar{e} \longrightarrow [\mathrm{FeCp_2}]^{+*} + 2\bar{e}, \qquad (1)$$

$$[\mathrm{FeCp_2}]^{+} + \bar{e} \longrightarrow [\mathrm{FeCp_2}]^{*}$$

$$\longrightarrow \mathrm{Fe}^{*} + [\mathrm{Cp}]^{*} + [\mathrm{Cp}], \qquad (2)$$

$$\mathrm{Fe}^{*} \longrightarrow \mathrm{Fe}^{0} + h\nu, \qquad (3)$$

$$[\mathrm{FeCp_2}]^{+} + \mathrm{FeCp_2} \longrightarrow [\mathrm{CpFeCpFeCp}]^{+} + [\mathrm{Cp}]. \qquad (4)$$

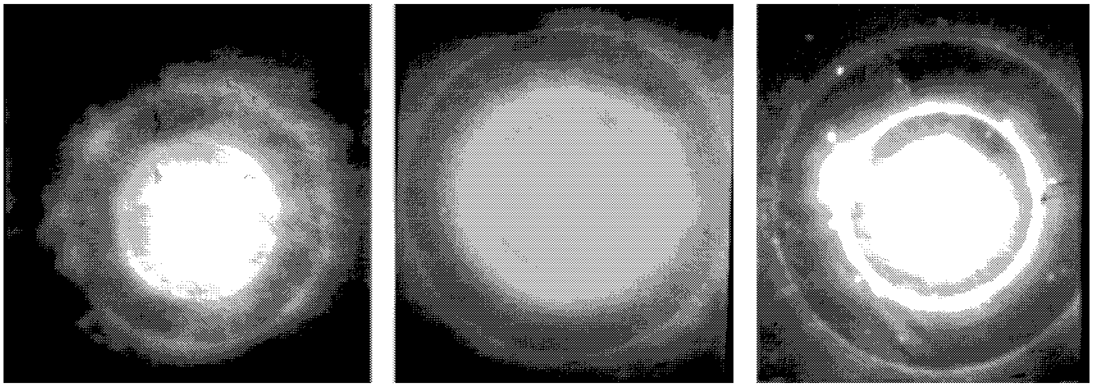
As noted in [1], in our conditions still more complex iron-containing ions may well form, close in composition to the starting ferrocene molecule. Recombination of simple and more complex iron-containing ions with plasma electrons would lead to precipitation of plasmochemically polymerized films close in element composition to the starting ferrocene. Most likely, the $[\mathrm{Cp}]^{\cdot}$ radicals undergo partial decomposition in the gas phase to form carbon-containing fragment ions. This is evidenced by the appearance of weak absorption bands in the IR spectra of plasmochemically polymerized ferrocene.

The spectrum of the plasmochemically polymerized film shows a broad band of medium intensity and complex structure at 2800–2950 cm^{-1}, assignable to aliphatic C–H stretching vibration bands. The weak bands at 1365, 960, 915, 890, 670, and 650 cm^{-1} are associated with polycyclopentadiene present in the film. The bands at 1050 and 1020 cm^{-1} (C–C stretching vibrations) and 1450, 1350, 870, 780, and 700 cm^{-1} (C–H bending vibrations) point to the presence of hydrocarbons which are presumably formed by decomposition of the cyclopentadienyl ring. We failed to establish the structure of this compound. Part of the cyclopentadienyl ring fragments together with iron atoms are incorporated into the growing plasmochemically polymerized ferrocene film, whereas other part leaves the reaction zone as gaseous compounds. This is a probable explanation for the slight disbalance of the element composition of plasmochemically polymerized ferrocene films compared with that of ferrocene [1]. However, the above decomposition contributes very little and has almost no effect on the composition of the film, as evidenced by comparison of the IR spectra of ferrocene and plasmochemically polymerized ferrocene films.

Along with the IR spectra, we also studied structural changes and crystallization dynamics of the films on exposure to electron beam. The crystal structure and phase composition of the crystallized film were determined by electron diffraction. The reference diffraction pattern measured in the beginning of film examination (Fig. 2a) showed that the film is amorphous. Crystallization began on 5-min exposure. The size of "grains" or "blocks" at the initial stage of crystallization was 50–100 Å. On further exposure the block size increased to 300–500 Å, together with enlarging crystallization field. The microdiffraction pattern of the film, measured after 20-min exposure, revealed Debye semirings (Fig. 2b). The observation of Debye semirings point to a polycrystalline structure of the surface layer of the chosen film segment and implies increased structural perfection of the film (appearance of disordered crystallographic planes). Further exposure resulted in faster crystallization (10–15 s), whereas the grain size did not change significantly. The diffraction pattern of this film segment (Fig. 2c) revealed two crystal structures, poly- and monocrystalline. The presence of the monocrystalline structure is evidenced by the appearance of reflexes on the diffraction pattern. A conclusion thus follows that this film segment has crystallized. The polycrystalline structure comprises fine crystals of iron oxides and $\mathrm{Fe_3C}$. The monocrystalline structure could be assessed with confidence. Further exposure produced no changes in the diffraction pattern, implying stabilization of the resulting structure.

EXPERIMENTAL

Plasmochemically polymerized ferrocene films were obtained as described in [1].



(a) (b) (c)

Fig. 2. Diffraction pattern of the plasmochemically polymerized ferrocene film. (a) Initial state, (b) initial crystallization stage, and (c) final crystallization stage.

The IR spectra were obtained on a Perkin–Elmer-577 spectrometer. Plasmochemically polymerized ferrocene films on KBr plate supports were placed in the working channel of the spectrometer.

The dynamics of crystallization of plasmochemically polymerized ferrocene films under electron beam was followed on a UEMV-200 microscope. Cubic NaCl supports with deposited plasmochemically polymerized ferrocene films were dissolved in water, and the films were deposited on the specimen grating of the microscope. The resulting samples were exposed to electron beam (accelerating voltage U 125 kV). The subsequent crystallization of the films occurred at an accelerating voltage of 150 kV.

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