Nanocomposites of Amorphous Hydrogenated Carbon and Siloxane Networks Produced by PECVD

B. Cláudio Trasferetti, Rogério V. Gelamo, F. Paulo Rouxinol, and Mário A. Bica de Moraes*

Instituto de Física "Gleb Wataghin", Universidade Estadual de Campinas, Caixa Postal 6165, CEP-13083-970, Campinas SP, Brazil

Maria do Carmo Gonçalves and Celso U. Davanzo

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, CEP-13.083-970, Campinas SP, Brazil

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It is well-known that siloxane networks can be prepared by plasma-enhanced chemical vapor deposition (PECVD) of silicon-containing molecular precursors.[1−4] PECVD is also a very suitable technique for depositing carbonaceous materials from organic molecular precursors.[5−7] However, little work has been done on the plasma deposition of hybrid materials constituted by inorganic and organic or carbonaceous polymeric networks. It is a general idea that PECVD is a technique that generates amorphous, coherent, and homogeneous random networks, even if plasmas of mixtures of two or more gases are used, but is this still true if the deposition is made from plasmas of both organic and silicon-containing molecules? In attempting to answer to this question, we used plasmas of hexamethyldisiloxane−acetylene−argon (HMDSO−AC−Ar) mixtures to deposit films in different conditions. We observed that, indeed, for some deposition parameters, phase separation occurs in the films, as revealed by transmission electron microscopy (TEM). Furthermore, from infrared (IR) measurements, we also observed that phase separation was suggested by the line shape analysis of the IR spectra.

The results of the TEM and IR spectroscopy analysis of the films are reported in this communication. The choice of HMDSO and acetylene relies on the fact that both are commonly used precursors in PECVD. Argon was used as a dilution gas. HMDSO already contains a stable Si−O−Si group, and it is thus very useful to obtain SiO_x-like materials. Furthermore, it has advantages such as relatively high vapor pressure, meaning that its vapor can be easily transferred to the plasma chamber, low toxicity (especially when compared to silane), and have low cost.[8] Acetylene is a precursor for carbonaceous materials, and from a suitable choice of the deposition parameters, a soft, highly cross-linked polymer[6] or a hard, diamondlike material[5] may be produced.

Table 1. Film Deposition Parameters

sample	$F_{C_2H_2}$ (sccm)	P_{HMDSO} (Pa)	F_{Ar} (sccm)
A1K and A1P	0	2.5	40
A2K and A2P	10	1.0	32
A3K and A3P	10	0.5	43
A4K and A4P	10	0	47

The films were deposited from radio frequency (rf) plasmas using a PECVD reactor described in a previous paper.[3] Oxygen and argon were admitted into the chamber reactor using precision mass flowmeters while the pressure was measured by a capacitance manometer. To admit HMDSO, an evaporation cell[2,3] was used. Keeping the same rf power (50 W), four different conditions of mass flow rates and pressures were used to obtain the films, as given in Table 1. The argon flow rate changed to keep the total pressure inside the chamber constant at 3.2 Pa. Therefore, all samples were deposited at the same total pressure. Parlodium-coated grids and KBr disks were used as substrates: the former to obtain the TEM images and the latter for the IR analysis. Typical thickness values for the films on parlodium-coated grids and KBr disks were 60 and 800 nm, respectively. We have found that 60 nm was an optimum thickness for acquisition of the TEM images. Films of higher thicknesses resulted in dark, poor-contrast images. The samples were labeled according to the substrate used, with K standing for KBr and P for Parlodium-coated grids.

TEM examinations of the films were carried out in a Zeiss CEM902 microscope, operating at 80 keV. The samples for TEM were stained with osmium tetroxide vapors for 12 h prior to the analysis. This is a useful procedure to check if an a-C:H phase containing carbon−carbon double and triple bonds coexist with other phases in the film. Osmium tetroxide reacts with the carbon−carbon double or triple bonds in unsaturated phases, thus enhancing the contrast in the TEM images due to the high scattering power of osmium.[9]

The infrared transmission spectra were obtained with a Bomen MB-101 FT-IR spectrometer equipped with a DTGS detector, having the spectrum of the bare KBr substrate as a reference.

Samples A1P through A4P were examined by TEM before and after exposure to OsO_4. Micrographs of the samples before exposure and sample A1P after exposure

* Corresponding author. E-mail: bmoraes@ifi.unicamp.br.

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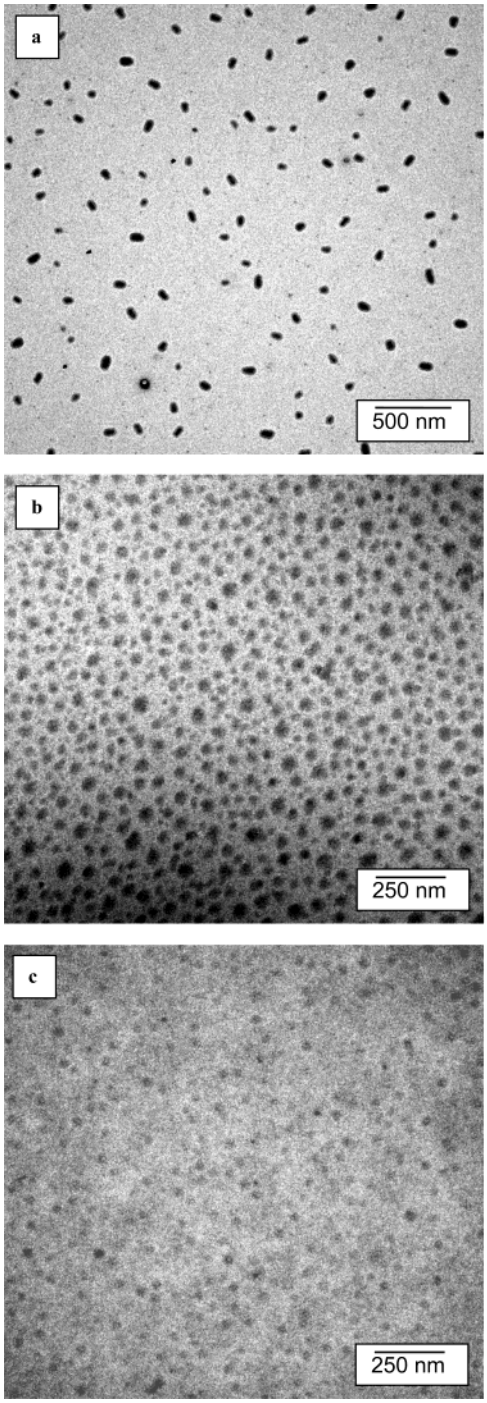

Figure 1. Transmission electron microscopy pictures of samples A2P (a), A3P (b), and A4P (c).

were continuous and did not suggest a structure or phase separation and therefore are not shown here. However, as shown in Figure 1, the micrographs of samples A2P and A3P after exposure clearly reveal a discontinuous film structure with one of the phases consisting of nanometric domains (dark spots) dispersed in the film volume (clear regions). Since the domains can be observed only after OsO_4 exposure, it can be concluded that they are actually formed by a hydrogenated amorphous carbon (a-C:H) phase. Clearly, the absence of these domains or any other structure in sample A1P was in fact expected since a single monomer (HMDSO) mixed with Ar was used in their preparation. From Figure 1, the volume fraction of the a-C:H phase

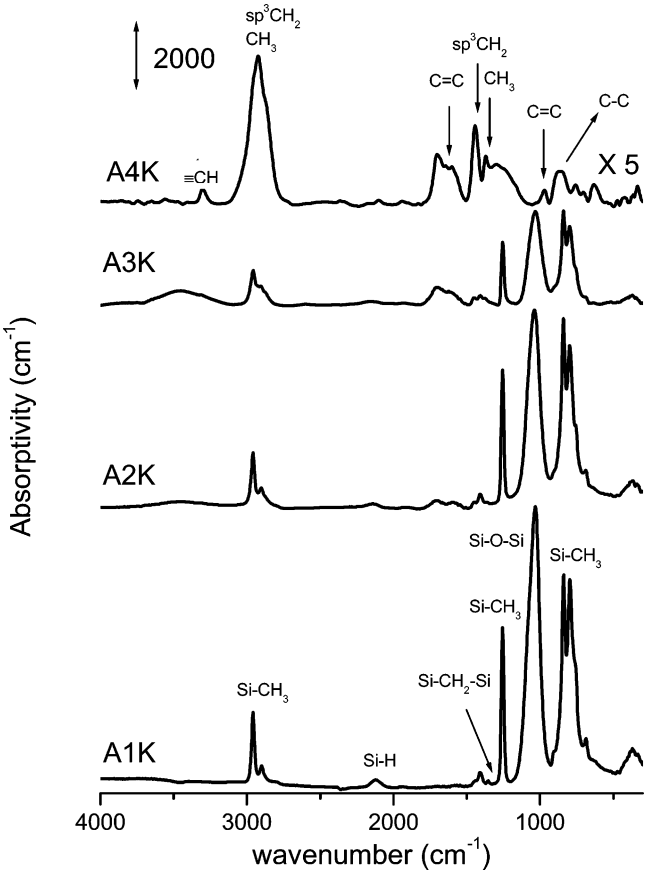

Figure 2. Infrared spectra of samples A1K through A4K.

is higher in sample A3P. This is due to the larger proportion of acetylene in the plasma as compared to that used to prepare sample A3P. It is important to remark that the sample A4P (Figure 1c) presents a certain contrast which may be due to the presence of both saturated and unsaturated carbon within its network, although the contrast is not as clear-cut as for the films deposited from HMDSO−AC−Ar mixtures. The dark spots shown in Figure 1c could be, in principle, interpreted as indicative of surface nucleation, a typically observed effect in films of various materials, in the early stages of film growth.[10] This is not the case in sample A4P since its carbon content is the highest, and thus the size of the dark spots would appear much larger in the micrograph. The formation of the a-C:H grains is thus a bulk phenomenon.

Infrared absorptivity spectra of samples A1K through A4K are shown in Figure 2. Band assignments for samples A1K and A4K were made according to the literature[11,12] and are presented in the Supporting Information. Such assignments show that the film deposited from the AC−Ar mixture (sample A4K) is a very complex material containing carbon with sp^1, sp^2, and sp^3 hybridizations. There are also C−H bonds in carbon atoms in all these hybridization states. The film deposited from a HMDSO−Ar mixture (sample A1K) is a highly cross-linked methylsiloxane network with a few methylene bridges. The spectra of the films deposited

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from HMDSO−AC−Ar mixtures (samples A2K and A3K) reveal the incorporation of chemical groups present in the films deposited from a single monomer (samples A1K and A4K). It is interesting to remark that the positions of the bands related to Si-containing moieties, for example, the asymmetrical stretching of Si−O−Si group (1025 cm^{-1}), are very steady regardless of the presence of AC in the plasma. Furthermore, the appearance of new bands related to Si−C groups was not observed for samples deposited from the HMDSO−AC−Ar mixtures. This suggests that the local chemical environment of silicon atoms is very similar for all samples, which is more consistent with the formation of two phases rather than a highly carbonated phase as the AC:HMDSO flow rate ratio increases in the discharge. Therefore, the IR data corroborate the inferences drawn from the micrographs.

A detailed description of the kinetics of the formation of our two-phase films is extremely difficult due to the large variety of molecular fragments in the plasma and their intrincate reaction paths both in the gas phase and at the surface of the growing film. Such a difficulty also holds for single-phase films. If C_2H_2 and HMDSO are simultaneously fed to the chamber, the fragments derived from C_2H_2 (organic fragments containing both saturated and unsaturated carbon species[13]) and from HMDSO (methylated siloxane and organic fragments[14]) are present in the discharge. Clearly, reactions between fragments generated from the same monomer and between those generated by the two monomers are possible. However, since the film is formed from reactions occurring at the substrate surface, and the TEM pictures exhibit a well-defined carbon-rich phase, a highly selective reaction scheme is indicated: reactions among species generated from the same monomer preferentially occur. It seems that the species containing unsaturated carbon are more reactive toward each other than toward silicon-containing species.

As reported by various investigators,[15] the polymer forming in a glow discharge process is closely related to the unsaturation of the monomer. For similar molecular weight monomers under identical conditions, the polymer deposition rate increases with increasing unsaturation. In view of these ideas it is possible that the fact that acetylene was used in the mixture with HMDSO, rather than a saturated hydrocarbon, favored the formation of the observed nanostructure, as the unsaturated species are more reactive toward each other and this would account for a more efficient formation of the carbon-rich grains.

Apparently, the same kind of selectivity applies for films obtained by PECVD from vinyltrimethylsilane (VTMS) in which a two-phase morphology has been observed.[16] From the scission of the bond formed between the silicon atom and the vinylic carbon of the VTMS molecule by the plasma, unsaturated carbon-containing fragments, such as $-C{=}CH_2$ and $-C{=}CH-$, can be formed. The observed phase separation in these films also seems to follow from the above-discussed selective reaction scheme.

Grill et al.[17] have obtained thin films from mixtures of tetramethylcyclotetrasiloxane and an organic monomer by PECVD. Although these films are precursors of nanoporous materials (obtained under thermal treatment of the as-deposited films), they have observed that the film structure is composed by a siloxane network to which fragments of the organic monomer are attached, that is, a structure fundamentally different from that observed in our films. Such a difference is not surprising since the mixtures and also the deposition system and deposition conditions are different. It is possible however that since the inorganic monomer used in ref 17 bears some similarity to HMDSO, the main reason for the difference remains in the organic monomer. Unfortunately, the latter is not revealed in ref 17.

Nanocomposite materials are currently desirable materials due to their prospective applications in biocompatibilization[18] and gas sensors,[19] for instance. Research on nanocomposite synthesis is a quickly growing branch of materials science and papers on that abound in the literature.[20] Our results point toward an expansion of the capabilities of PECVD, which is accessible and fully compatible with the present silicon technology, to the synthesis of nanocomposites. Further structural characterization and studies of the properties of these nanocomposites synthesized by PECVD are currently underway in our laboratory.

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Supporting Information Available: Band assignments for the films deposited from acetylene or HMDSO (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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