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ArF laser photolysis of gaseous CS_2–$(CH_3)_4Sn$ mixtures: gas-phase reaction between tin and sulfur and deposition of nanosized tin sulfides incorporated in a polymer network†

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ArF laser photolysis of gaseous $(CH_3)_4Sn$–CS_2 mixtures results in chemical vapour deposition of tin sulfides (SnS and SnS_2) incorporated in a network of a blend of polythiene and organotin polymers. The evidence for the tin sulfides was obtained by examination of the deposited coatings by infrared spectroscopy, Raman spectroscopy and electron microscopy. The formation of tin sulfides is explained by reaction of transiently generated Sn and S atoms. The reported results reveal for the first time that nanosized clusters of Sn and S produced in the gas phase react into tin sulfides at ambient temperature of the gas phase.

Introduction

ArF laser photolysis of gaseous carbon disulfide takes place *via* single- and double-photon excitation and results[1–5] in the transient formation of energy-rich (excited) CS fragments and S atoms that allow[6] chemical vapour deposition of polythiene $(CS)_n$ polymer and S_n. This photolytic polymerisation of CS is a unique process, since it differs from the earlier reported CS polymerisation through a heterogeneous wall reaction in the absence of UV excitation, leading[7] to a carbonaceous polymer.

The transient occurrence of the CS fragments and S atoms makes it appealing to use this photolysis as a source of these species to study their reactions with other reaction partners. Such experiments have not been, however, yet been reported. This might be due to the fact that some reaction partners can inhibit CS_2 dissociation, as happens in the ArF laser co-photolysis of CS_2 and ethene in which ethene reacts with $(CS_2)_n$ (n = 2,3) agglomerates to yield a C/S/H copolymer with $(CS_2)_n$ moieties separated by $–CH_2CH_2–$ links.[8,9]

The ArF laser photolysis of gaseous tetramethyltin is known to occur *via* a sequential splitting of the methyl groups to yield $(CH_3)_nSn$ (n = 1–3) fragments, together with a large distribution of ground and excited state Sn atoms, resulting in chemical vapour deposition of organotin polymer.[10] Should this photolysis occur simultaneously with the photolytic dissociation of CS_2 into CS and S, it might be possible to react the gas-phase generated S and Sn species and enable formation of an organotin and polythiene polymer.

There is enormous interest in the synthesis of nanosized metal chalcogenides at low (room) temperatures[11] and ongoing attention is paid to fabrication of semiconductor nanocomposites in polymeric networks.[12,13] Nanosized metal chalcogenide particles dispersed within polymer matrices are the subject of ongoing research[14–17] due to their unique electronic and optical properties and potential applications in solar energy conversion, photoconducting cells and nonlinear optics.

We have decided to examine the ArF laser photolysis of gaseous CS_2–$(CH_3)_4Sn$ mixtures and to determine whether it procures conditions for room-temperature gas-phase synthesis of nanosized tin sulfides and their protection (stabilization) by concurrently polymerising CS and $(CH_3)_nSn$ species.

In this work we examined, by X-ray photoelectron spectroscopy, Raman spectroscopy, infrared spectroscopy and electron microscopy, the final products obtained by chemical vapour deposition from the ArF laser photolysis of gaseous CS_2–$(CH_3)_4Sn$ mixtures. We give the first (although indirect) evidence on the gas-phase reaction between Sn and S clusters yielding SnS and SnS_2 at room temperature of the gas phase.

Experimental

The ArF laser photolytic experiments were carried out on gaseous mixtures of CS_2 (10–20 Torr) and $(CH_3)_4Sn$ (10–20 Torr) in He (total pressure 760 Torr) using an ELI 94 laser operating at 193 nm with a pulse energy of 60 mJ incident on 2.3 cm^2 and a repetition frequency of 10 Hz. The laser beam was mildly focused to achieve incident fluences of 130–340 mJ cm^{-2}. The gaseous samples were irradiated in a Pyrex reactor (140 ml in volume), which was equipped with a sleeve with a rubber septum and PTFE valve connecting it to a standard vacuum manifold and consisted of two orthogonally positioned Pyrex tubes, one fitted with two quartz plates and the other furnished with two NaCl windows. It accommodated metal (Al, Cu), KBr and quartz substrates, which, covered with the deposited solid material in the course of photolysis, were transferred for the X-ray photoelectron spectroscopy, Raman

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† Electronic supplementary information (ESI) available: FTIR spectra of the deposits. See http://www.rsc.org/suppdata/nj/b4/b418758j/

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spectroscopy and electron microscopy measurements. (The FTIR and UV spectra of the deposited solids were measured directly in the reactor.)

The progress of the photolysis was monitored by periodically removing the reactor from the laser irradiation section and placing it in the compartment of an FTIR (Nicolet Impact 400) spectrometer. The depletion of CS_2 and $(CH_3)_4Sn$ was determined using diagnostic bands at 2180 (CS_2) and 530 [$(CH_3)_4Sn$] cm^{-1}. The volatile products of the photolysis were examined by FTIR spectroscopy, coupled GC-MS (QP 1000 Shimadzu mass spectrometer) and quantified by gas chromatography (Shimadzu GC 14A gas chromatograph with FID detector coupled with a Chromatopac C-R5A computing integrator). Both instruments were equipped with Porapak P (1.5 m long) columns and operated at programmed temperature (20–120 °C) using He carrier gas.

The FTIR spectra of the deposited solid films were recorded after prolonged evacuation of the reactor.

Raman spectra were measured on a Renishaw (a Ramascope model 1000) Raman microscope coupled with a CCD detector. The exciting beam of an Ar ion laser was defocused to obtain an energy density of *ca.* 10^2–10^3 W cm^{-2} and to diminish the heating of the sample.

SEM images were obtained using a Philips XL30 CP scanning electron microscope. TEM analysis (particle size and phase analysis) was conducted on a Philips 201 transmission electron microscope at 80 kV on deposited materials scraped from the metal substrates and transferred to a Formvar 1595 E (Merck) membrane-coated Cu grid. Process diffraction[18] was used to evaluate and compare measured electron diffraction patterns with an XRD diffraction database.[19]

Carbon disulfide (99.9% purity) and tetramethyltin (95% purity) were purchased from Aldrich and were distilled prior to use.

Results and discussion

The ArF laser photolysis of gaseous CS_2–$(CH_3)_4Sn$ mixtures in He results in depletion of both components, the formation of volatile hydrocarbons and deposition of a yellowish solid coating on the bottom of the reactor. The distribution of the hydrocarbons [in relative molar percent: CH_4 (40–45), C_2H_4 (2–4) and C_2H_6 (51–54)] is practically independent of the laser fluence used. No volatile tin- and sulfur-containing products were observed, which is in agreement with (i) a complete use of CS_2 for the formation of solid deposit and (ii) the previous observation that the photolysis of $(CH_3)_4Sn$ yields[10] $Sn(CH_3)_n$ (n = 0–3) fragments producing solid organotin films. The observed formation of CH_4 and C_2H_6 is in keeping, respectively, with H-abstraction from $(CH_3)_4Sn$ by the CH_3 radical and combination of the CH_3 radicals. The comparable amounts of both hydrocarbons indicate that both steps are of similar importance.

The yellowish films deposited at incident fluences of 130–340 mJ cm^{-2} show very similar SEM images and an example is given in Fig. 1. Their morphology [Fig. 1(a) and 1(c)] differs from that of the deposit obtained from the ArF laser photolysis of $(CH_3)_4Sn$ [Fig. 1(b)] and resembles that of the deposit from the ArF laser photolysis of CS_2 (ref. 6). TEM images (Fig. 2) show nano-chain-like agglomerates whose size becomes smaller with higher laser fluence: 10–20 nm and *ca.* 100 nm large particles are seen at fluences (f) of 340 and 140 mJ cm^{-2}, respectively. The EDX analysis of the solids reveals the presence of the elements C, S, Sn and O and their stoichiometry determined for the solids obtained from equimolar amounts of both gases at f = 140 and 340 mJ cm^{-2} ($C_{1.00}S_{0.78–0.88}Sn_{0.75–0.94}$) is compatible with the rather similar content of C, S and Sn atoms implying a very efficient removal of CH_3 groups from $(CH_3)_4Sn$. Some oxidation of the films took place during their transfer to the electron microscope.

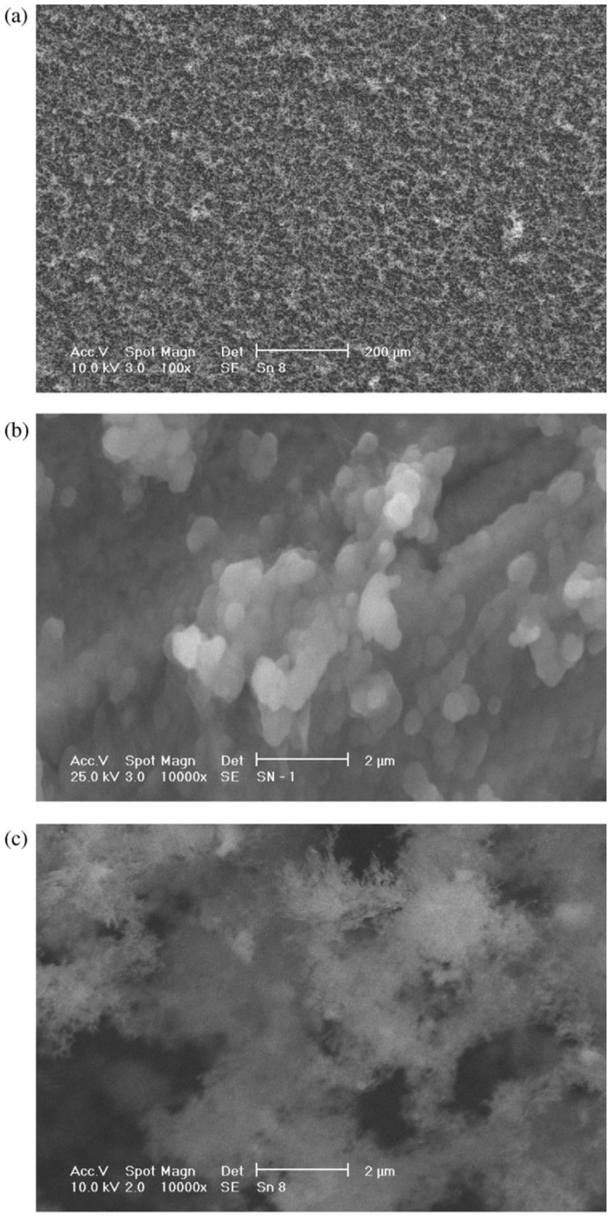


Fig. 1 Typical SEM images of the deposit from photolysis of CS_2–$(CH_3)_4Sn$ (10 Torr each , f = 130 mJ cm^{-2}) and of the deposit from photolysis of pure $(CH_3)_4Sn$ (10 Torr, f = 130 mJ cm^{-2}) given for the sake of comparison. The bar lengths are: (a) 200, (b) 5 and (c) 5 μm.

FTIR spectra (in the electronic supplementary material) of the solids indicate contributions of several vibrational modes. Their detailed assignment for the deposits obtained under different irradiation conditions is given in Table 1. The spectra show several structures observed[6] in polythiene films [ν_s(C=S),

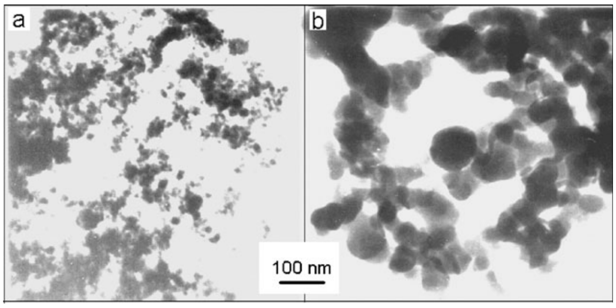


Fig. 2 TEM images of the deposit from the photolysis of CS_2–$(CH_3)_4Sn$ (10 Torr each) as a function of f: (a) 340 and (b) 130 mJ cm^{-2}.

Table 1 FTIR spectra of deposited solids obtained from CS_2–$(CH_3)_4Sn$ mixtures under different irradiation conditions[a]

	Absorbance intensity[b] of the different mixtures				
Wavenumber/ cm^{-1}	A	B	C	D	Assignment[16–22]
2990 (±5)	0.10	0.13	0.12	0.25	ν(C–H)
2925 (±8)	0.22	0.12	0.11	0.32	
2876 (±6)	0.06	0.02	0.04	0.07	
1538 (±3)	0.10	0.60	0.71	0.90	$\nu(C{=}C)S_n$ (n = 1, 2)
1371 (±5)	0.12	0.10	0.05	0.11	$\nu(C{=}C)S_4$
1210 (±2)	1.00	1.00	1.00	1.00	$\nu_{as}(C{-}C) + \nu_s(C{=}S) + \delta(C{-}H)$
1186 (±6)					
1139 (±0)	1.00	0.98	0.99	0.97	$\nu_{as}(C{-}C) + \nu_s(C{=}S)$ in –C–(C═S)–S– + $\delta(C{-}H)$
1093 (±3)	0.20		0.25	0.11	$\nu_s(C{=}S)$ in –S–(C═S)–S–
1038 (±3)	0.61	0.84	0.71	0.79	$\nu_s(C{=}S)$
990 (±3)	0.11	Sh			$\nu_{as}(C{-}S) + \delta(Sn{-}H)$
947 (±3)		0.14	0.12		$\nu_s(C{-}C) + \delta(Sn{-}H)$
907 (±0)					$\nu_{as}(C{-}C{-}S)$
872 (±6)	0.10			0.02	$\nu_{as}(S{-}C{-}S)$
807 (±1)	Sh				$\delta({=}C{-}H) + \nu_{as}(S{-}C{-}S)$
777 (±1)	0.83	0.53	0.60	0.86	$\rho(C{-}H) + \nu_s[-C{-}({=}C){-}C]$
673 (±2)	0.15				$\nu_s(C{-}S) + \nu_s[-C{-}({=}C){-}C]$
606 (±2)	0.21	0.35	0.39	0.37	$\nu(Sn{=}S)$
547 (±0)	0.18	Sh	Sh	Sh	$\nu_{as}(Sn{-}C) + \nu_s(C{-}C{-}S) + \nu(Sn{=}S)$
529 (±1)	0.20		0.48	0.73	$\nu_s(Sn{-}C) + \delta[-C({=}C){-}C]$
475 (±2)	0.09	0.15			$\nu_s(S{-}C{-}S)$
449 (±6)	0.18			0.55	$\delta[-C{-}({=}C){-}C]$
419 (±3)	0.20	0.64	0.74	0.08	$\nu(S{-}S) + \nu(Sn{=}S)$

[a] A: f = 130 mJ cm^{-2}, CS_2 (10 Torr), $(CH_3)_4Sn$ (10 Torr); B: f = 280 mJ cm^{-2}, CS_2 (10 Torr), $(CH_3)_4Sn$ (20 Torr); C: f = 290 mJ cm^{-2}, CS_2 (20 Torr), $(CH_3)_4Sn$ (20 Torr); D: f = 340 mJ cm^{-2}, CS_2 (10 Torr), $(CH_3)_4Sn$ (10 Torr). [b] Normalized to absorbance of the band due to the $\nu_{as}(C{-}C)$, $\nu_s(C{=}S)$ and $\delta(C{-}H)$, $\nu(C{-}C)$ modes at 1210 (±2) cm^{-1}.

$\nu(C{=}C)S_n$] and $H_nC{-}Sn$ structures.[20,21] They also indicate Sn═S bonds in SnS and/or SnS_2 tin sulfides[22,23] and S–S bonds in C–SS–C structures.[24] The occurrence of sulfur allotropes having absorptions at 411 and 471 cm^{-1} (S_8)[25] and 402 and 476 cm^{-1} (S_7)[26] observed in the solids from the ArF laser photolysis of CS_2 was not confirmed.

The Raman spectra of the solids (example in Fig. 3) are more diagnostic and show peaks at 1430–1470 and 1197–1203 cm^{-1} [respectively assignable[6] to $\nu(C{=}C)$ and $\nu(C{=}S)$ in $(S_2)C{=}C(S_2)$ configurations], a peak at 517–525 cm^{-1} [corresponding to the $\nu_s(Sn{-}C)$ mode in organotin moieties[16]] and peaks at 307 and 340–360 cm^{-1} that are, respectively attributable[27,28] to the A_{1g} and A_{2u} (TO, LO) modes in SnS_2.

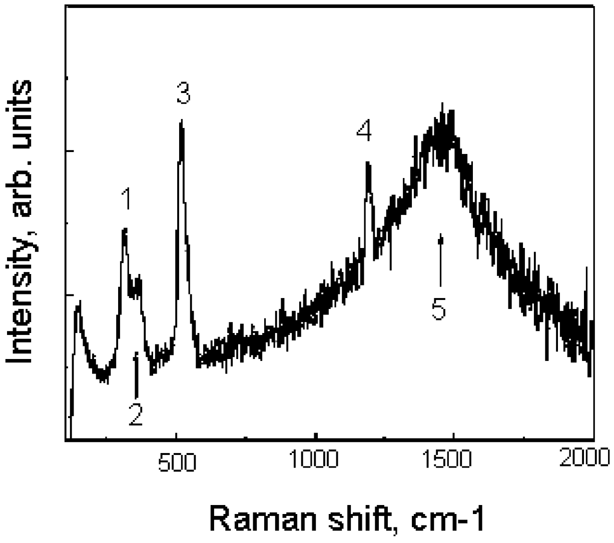


Fig. 3 Typical Raman spectrum of the deposit. The designated bands 1–5 are located, in the given order, at 307, 340–360, 517–525, 1197–1203 and 1430–1470 cm^{-1}.

Another piece of evidence for the presence of a tin sulfide is provided by the electron diffraction patterns of the selected samples (*e.g.*, Fig. 4) that reveal the presence of the crystalline SnS phase.

These complementary Raman spectral and ED analyses are in keeping with SnS_2 being (at least mostly) in an amorphous state, while SnS, not so abundant, is present in the crystalline state.

All of the analytical data on the solid deposits show that the solids are a blend of C/S polymer (formed[6] from the polymerisation of the CS radicals) and an organotin polymer [produced from the $(CH)_3Sn$ (n = 1,2) fragments generated[10] from the photolysis of $(CH_3)_4Sn$] that contains SnS and SnS_2 tin sulfides.

We explain the formation of the tin sulfides by a direct reaction between nanosized clusters of elemental tin and sulfur. These clusters, along with the polythiene and organotin polymers, are produced by known[6,10] reactions (Sn–C and C–S fission, H-abstraction by and combination of CH_3 radicals, combination of methylene, and polymerisation of Sn- and C-centred radical species and carbon sulfide (Scheme 1). We

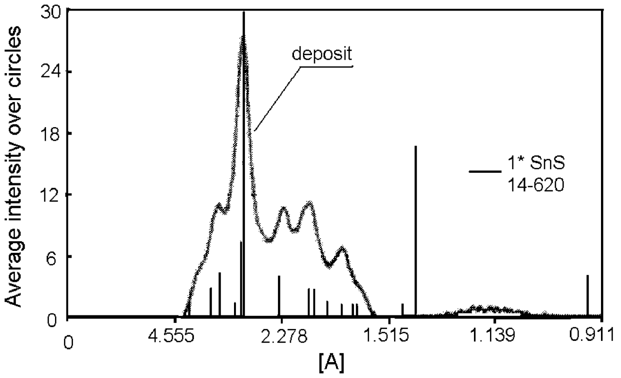
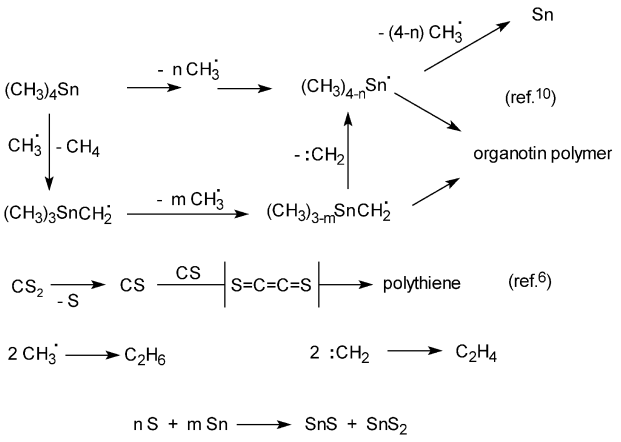


Fig. 4 Typical diffraction pattern of the deposit compared with the SnS diffraction pattern from the XRD diffraction database.[19]



Scheme 1

remark that the steps involving methyl radicals were reported not only for the ArF laser photolysis[10] but also for the surface-free thermal decomposition[29] of tetramethyltin.

This scheme is supported by the absence of elemental S in the deposit. We assume that the elemental sulfur (observed in the photolysis of CS_2, ref. 6) must have been lost by a sink reaction with Sn.

We point out that our data give the first, though indirect experimental evidence for the formation of nanosized tin sulfides from clusters of Sn and S at bulk ambient temperature of the gas phase. This reaction is feasible due to the small size of the reacting species and the negative heats of formation of tin sulfides. This reaction between the Sn and S clusters contributes to the number of available methods for the synthesis of tin sulfides, which are normally prepared at very high temperatures or by solvothermal routes (*e.g.* refs. 30 and 31). We point out that the photolytic generation of small clusters of metals and chalcogenides in the gas phase can procure conditions for the chemical vapour deposition of metal chalcogenides at room temperature of the gas phase. Our finding extends our recent report[11] on the room-temperature reaction between some metals and laser-generated selenium.

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