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Samarium Dithiocarbamates as Precursors for Deposition of SmS Films

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Abstract — Samarium dithiocarbamate complexes dtc_3Sm and their adducts dtc_3SmL were prepared, studied, and used as precursors for deposition of SmS films. The influence of the composition and structure of the complexes on the properties of the SmS films was examined.

Samarium monosulfide shows promise for development of various thin-film components for opto- and microelectronic devices. SmS films are an active medium for optical information recording with a laser beam, owing to occurrence of the metal–semiconductor phase transition [1]. In addition, these compounds exhibit ultrahigh strain sensitivity, which allows their use as highly sensitive strain sensors [2]. However, SmS films are prepared today exclusively by vacuum methods, which do not yet ensure the required stability and reproducibility of the characteristics. Therefore, the existing procedures for film preparation should be improved, or new, more efficient procedures should be developed.

At the same time, in deposition of semiconducting films, chemical methods in most cases are advantageous as compared to vacuum deposition. Therefore, development of chemical procedures for deposition of SmS films is an urgent problem. Published data on sulfur-containing samarium compounds suitable for preparing SmS silms are extremely scarce [3, 4], and systematic studies are not pursued in this field.

We were the first to reach a success in deposition of SmS films from samarium diethyldithiocarbamates [5–7]. These studies mainly concerned the conditions of growth, structure, and properties of films of samarium sulfides, including SmS. However, the synthesis and properties (relevant to the growth parameters and properties of the films) of the starting compounds were not studied in detail.

The goal of this work was examination of synthesis conditions and study of properties of samarium dithiocarbamates obtained by various procedures, and also examination of the influence exerted by the structure of the starting compounds on the properties of SmS films obtained by their pyrolysis.

It was interesting to examine the possibility of preparing Sm dtc complexes from aqueous solutions of a samarium salt and dtcNa, since dithiocarbamates of cadmium, zinc, indium, and some other metals, used for deposition of polycrystalline films of CdS, ZnS, In_2S_3, Cu_xS, etc. [8], can be prepared by such a procedure. Semiconducting materials are formed by thermolysis of dithiocarbamates at relatively low temperatures (200–300°C) in air. Neither synthesis nor pyrolysis of the starting compounds require sophisticated equipment.

However, we failed to prepare samarium dithiocarbamate by the standard procedure involving reaction of the metal salt [$SmCl_3$ or $Sm(NO_3)_3$] with dtcNa in 1 : 3 ratio in aqueous solution [3].

To find conditions for preparing the complex, we varied the concentrations and ratios of reactants and added H_2O_2 to prevent reduction of Sm(III) to Sm(II). The results are listed in the table. It is seen that, on adding H_2O_2 in the amount varied in a wide range (from 0.05 to 1.25 ml of 3% H_2O_2 per 100 ml of solution), with the concentrations of the reactants being the same as usually used for preparing dtc complexes of other metals, the desired complex does not precipitate either. Variation of the reactant ratio, with the dtcNa concentration increased by a factor of 4 from 0.025 to 0.1 M, without adding H_2O_2, resulted in precipitation of a small amount of the product (sample no. 1). Addition of H_2O_2 (batch I) substantially increased the product yield, which reached 12% for

Effect of the synthesis conditions on formation of the samarium(III) complex in aqueous solution

Batch	Sample no.	c_{SmCl_3}, M	c_{dtcNa}, M	$SmCl_3$: dtcNa	$c_{H_2O_2}$, ml	Characteristics of complex	T_t, °C[a]
I	1	0.025	0.1	1 : 4	–	Traces	–
	2	0.025	0.1	1 : 4	0.12	Light yellow	–
	3	0.025	0.1	1 : 4	0.30	White	–
	4	0.025	0.25	1 : 10	1.00	Gray	–
II	5	0.025	0.1	1 : 4	1.25	White loose[b]	80, 180, 270
	6	0.025	0.1	1 : 4	5.00	Gray-lettuce dense[c]	70, 260
	7	0.025	0.1	1 : 4	2.50	Light lettuce loose[b]	75, 80, 230
	8	0.025	0.1	1 : 4	0.75	White loose[b]	75, 200, 270
III	9	0.025	0.25	1 : 10	4.00	″	80, 270
	10	0.025	0.25	1 : 10	12.00	Lettuce, very loose[b]	80, 270
	11	0.025	0.25	1 : 10	24.00	Yellow-green loose[c]	80, 220
IV	12	2.0	2.0	1 : 1	–	Yellow loose[d]	170, 380
	13	2.0	2.0	1 : 2	–	Yellow dense[b]	170, 200, 380
	14	2.0	2.0	1 : 4	–	White loose[b]	150, 200, 380
	15	0.8	0.8	1 : 2	–	Yellow dense[b]	170, 380

[a] (T_t) Transition point. [b] Amorphous decomposition products were not identified. [c] The major decomposition product is samarium oxysulfide. [d] The major decomposition product is samarium sulfide.

sample no. 2 and 55% for sample no. 3. However, when the content of dtcNa was further increased by a factor of 2.5 and the content of H_2O_2, by a factor of 3.3, the product yield increased only slightly (sample no. 4).

In another series of experiments (batch II), at a significant (fourfold) excess of dtcNa, the H_2O_2 content was varied from 0.75 to 5.0 ml of 3% H_2O_2 per 100 ml of the solution of the reactants. In these experiments, we obtained precipitates in a high yield (~60%, sample nos. 5–8).

In batch III, the dtcNa content was increased by a factor of 10. In this series of experiments, the product yield also tended to grow with increasing content of H_2O_2. However, the yield and quality of the products were, on the whole, similar to those of sample nos. 5–8. Thus, the fourfold excess of dtcNa can be considered as an optimum. Since the above results show that the yield and quality of the reaction product depend not only on the ratio of the reactants but also on their absolute concentration in solution, in experimental series IV we examined the possibility of preparing samarium dtc complexes at higher concentrations of the reactants without adding H_2O_2. Experiments show that the synthesis can be successful not only at high (2 M, sample nos. 12–14) but also at moderate (0.8 M, sample no. 15) concentrations of the reactants.

As judged from the color and density of the precipitates (see table), different complexes are obtained depending on the synthesis conditions; formation of a mixture of complexes is also possible. This may be due both to the variable valence of samarium and to the influence exerted by the reactant concentration and ratio and also by the presence of water on the complexation. As a result, the steric arrangement of dtc ligands around the Sm ion may vary.

The complexes were studied by thermal analysis and volumetry, and solid products of their decomposition were identified by X-ray diffraction and elemental analysis.

The thermal analysis and volumetry revealed the occurrence of several thermal transitions (see table). The lowest-temperature transition is apparently indicative of the presence of water (sample nos. 5–11). The higher-temperature transitions are related to melting and decomposition, which are accompanied by vigorous gas evolution. However, the transition temperatures often appreciably differ from one sample to another. Samarium is present in the residue, but not only in the form of sulfides (sample no. 12) and oxysulfides, but also in other unknown forms (possibly, in the form of hydroxide). Apparently, the majority of the samples contain large amounts of impurities. Additional studies aimed to identify the impurities revealed formation of thiuram disulfide in some samples and of samarium hydroxide in most cases. Formation of $Sm(OH)_3$ is due to the fact that the synthesis is performed in aqueous solution and that the complex dtc_3Sm is apparently unstable and susceptible to hydrolysis. This process is the most probable when the ratio and especially concentration of the reactants are far from the optimum.

The IR spectra of batch IV samples contain a weak band at 1000 cm^{-1} characteristic of the metal–sulfur chelate bond in metal dtc complexes, obscured by the band at 980 cm^{-1} characteristic of dtcNa. The melting and decomposition points of these samples are considerably higher than those of the samples of the other batches and are close to the values expected for dtc$_3$Sm; these samples seem to be the most promising as precursors for film deposition. Since only a few samples of samarium complexes prepared in aqueous solution had the characteristics close to the required level, it was appropriate to examine the possibility of preparing the complexes in nonaqueous solution.

With the aim to prepare samarium dithiocarbamates in nonaqueous solution, we initially used the known procedure for preparing dithiocarbamates of some lanthanides, very briefly described in [3]. We have modified this procedure to prepare dtc$_3$Sm and also applied it to adducts of dtc$_3$Sm with neutral ligands. Samarium diethyldithiocarbamate was prepared from solutions of SmCl$_3$ and dtcNa in ethanol. All the manipulations were performed under argon.

In addition, we prepared Sm dtc complexes with additional ligands with the aim to increase the volatility of the complex, facilitate its transport to the support, and create sufficiently high vapor pressure in the vicinity of the support. Additional ligands, bipyridine (bipy) and phenanthroline (phen), saturate the inner coordination sphere of samarium, preventing oligomerization and hydration of the complexes.

All the synthesized compounds are virtually colorless. The complexes are soluble in acetonitrile, chloroform, and dichloromethane, with dtc$_3$Sm being better soluble in acetonitrile, and dtc$_3$Smbipy and dtc$_3$Sm · phen, in chloroform and dichloromethane. The complexes were recrystallized from appropriate solvents and subjected to thermal analysis and volumetry. Thermal decomposition of all the complexes occurs in the range 300–350°C with an endothermic effect. At 390°C, vigorous gas evolution is observed; the solid inorganic residue contains samarium sulfides.

In going from sodium dithiocarbamate to the samarium complex, the positions of the IR absorption bands and the shape of the IR spectrum as a whole change insignificantly. All the three types of compounds have an absorption band at about 1000 cm^{-1}, characteristic of dtc complexes. As follows from [9], in the case of chelate coordination of a dithiocarbamate ligand, there is a separate band at 1000 cm^{-1} belonding to vibrations of two equivalent C–S bonds. If the dithiocarbamate ligands are nonequivalent, this band splits (1005 and 983 cm^{-1}). The compounds dtc$_3$Sm and dtc$_3$Smphen in the region of 1000 cm^{-1} have the same set of three bands (980, 990, 995 cm^{-1}), and the bands of dtc$_3$Smbipy (985, 1000, 1005 cm^{-1}) virtually coincide with those given in [9].

In the IR spectrum of the phenanthroline complex, the band at 1000 cm^{-1} is present but is weak. However, all the bands belonging to the dithiocarbamate and phenanthroline ligands are present; the main phenanthroline bands are not noticeably shifted relative to the free ligand.

The data for free and coordinated bipyridine are nicely consistent with the results obtained for the related complexes of Mo, Sb, Bi, Ni, Er, and Ta [9].

Thus, examination of the complexes prepared in nonaqueous solutions showed that the majority of them have the required characteristics confirming formation of fairly pure samarium dithiocarbamates suitable as precursors for deposition of SmS films.

The film deposition by heterogeneous pyrolysis of samarium dithiocarbamates was performed by spraying a 0.1 M solution of the starting compound in pyridine onto a heated support. Due to simplicity of the installation and high rate of the film growth, this method allows relatively fast preparation of a large number of film samples under varied conditions.

We used four starting complexes: dtc$_3$Sm, dtc$_3$Sm · bipy, and dtc$_3$Smphen prepared from ethanolic solution under argon, and also dtc$_3$Sm prepared from aqueous solution.

In our experiments, we varied not only the precursors but also their concentration in solution (in the range 2–4 wt %), support temperature (180–300°C), vapor pressure (by varying, along with the precursor concentration, also the distance between the sprayer and support from 2 to 8 cm), diameter of the cylinder (60–120 mm), amount of the precursor to be sprayed, and spraying time. Along with the main solvent (pyridine), we added in some experiments diglyme and dimethylformamide in various ratios. The solvents in this case not only act as the carriers of the precursor compound, but also suppress side processes significantly affecting the composition and quality of the films.

The films were mainly deposited on Sitall (devitrified glass) supports. For comparison, some samples were prepared on polished silicon plates, single-crystalline mica supports, and NaCl with the growth surfaces. The overwhelming majority of samples were prepared in the steady-state spraying mode at the flux of the precursor of ~1 mg cm^{-2} min^{-1}; several samples were prepared at a small distance from the sprayer to the support (2–3 cm) and hence at a higher flux. Virtually all the films showed a high adhesion to the support.

Experiments on the film deposition showed that the starting compound significantly affects the growth parameters, structure, and surface morphology of the films.

One of the most important parameters is the film growth rate V. Figure 1 shows the dependence of V on the flux of the precursor I (per cm^2 of the support surface per minute) at a fixed temperature (namely, 240°C). It is seen that the highest growth rate is observed with the bipyridine ligand (curve *1*). With the phenanthroline ligand (curve *2*), the growth rate is slightly lower, and still lower it is without a neutral ligand (curve *3*). The complexes prepared from aqueous solution without neutral ligand also show appreciable rate of the film growth (curve *4*). Thus, all the types of complexes are sufficiently volatile to obtain pyrolytic films and are suitable as precursors for deposition of SmS films.

The optimal flux of the precursor, at which the resulting films are uniform with respect to thickness and color and are relatively fine-grained, is 0.75–1.25 mg cm^{-2} min^{-1}. At higher fluxes of the precursor (2.5–3.0 mg cm^{-3} min^{-1}), at which the film growth rate is considerably higher, the vapor in the vicinity of the support is considerably oversaturated and the mass transfer is not steady-state; the resulting films have a low surface resistivity (~10^3–10^4 Ω mm^2). Such values are characteristic of the metallic phase of SmS exhibiting the strain sensitivity. At the same time, films prepared under steady-state conditions at a flux of 0.75–1.25 mg cm^{-3} min^{-1}, as a rule, have a high surface resistivity (10^9–10^{11} Ω mm^2) characteristic of the semiconducting phase of SmS.

Examination of the crystal structure of the films showed that, in the temperature range tested, polycrystalline films are mainly formed. The highest degree of ordering of the crystallites is observed in the films prepared from dtc$_3$Smbipy. These are textured films of the cubic modification with the lattice constant ranging from 0.56 – 0.57 nm; such values are characteristic of SmS [1, 2]. The films prepared from dtc$_3$Smphen and also from dtc$_3$Sm synthesized under argon and in aqueous solution are also polycrystalline but have a less perfect structure.

The films prepared from the phenanthroline complex show a low degree of ordering in the entire range of deposition temperatures. This may be due to the fact that the bulkier phenanthroline ligand has no time to volatilize and is captured by the film-forming elements, preventing formation of crystallites on the support.

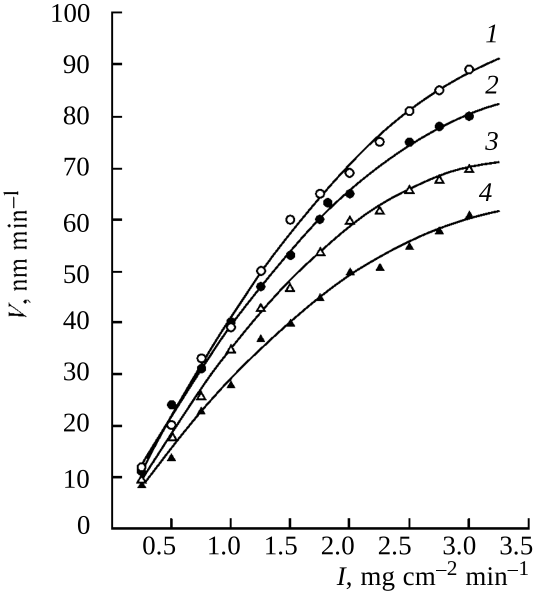

Fig. 1. Rate of film growth as a function of the flux of the precursor: (*1*) dtc$_3$Smbipy, (*2*) dtc$_3$Smphen, (*3*) dtc$_3$Sm (anhydrous medium), and (*4*) dtc$_3$Sm (aqueous medium).

When studying the crystal structure of the films, we revealed a significant effect of the support material: On mica (0001), as a rule, the degree of crystallite ordering was higher than on NaCl (001). The films prepared on polished silicon plates have the crystal structure that only slightly differs from the structure of the films deposited on amorphous Sitall, which may be due to the lack of the directing effect of the polished support surface.

An electron-microscopic study of the morphology of the film surface showed that the starting compounds and procedures for their preparation strongly affect the surface microrelief of the films prepared under similar conditions (Fig. 2). This effect is especially pronounced in the case of dtc$_3$Smphen (Fig. 2d) when a second SmS phase is formed as “domes” and “spheroids” 2–3 μm in diameter.

The elemental analysis performed by an X-ray fluorescence method using an X-ray microanalyzer shows that the films are not noticeably contaminated with carbon. Its content is on the level of the device sensitivity (~0.1%). However, the stoichiometric ratio of the elements widely varies, which contradicts the

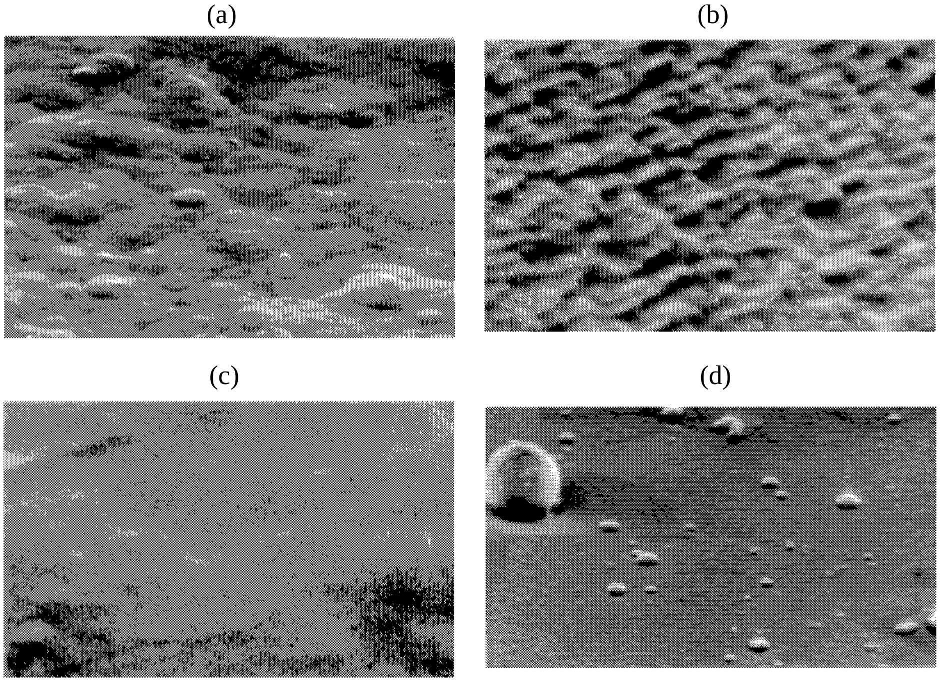

Fig. 2. Microrelief (magnification 5000×) of the surface of SmS films prepared from various precursors: (a) dtc_3Sm (nonaqueous medium), (b) dtc_3Sm (aqueous medium), (c) $dtc_3Smbipy$, and (d) $dtc_3Smphen$.

results of electron diffraction analysis and suggests the presence of uncontrollable impurities.

The composition of the solvent also significantly affects the film quality, but the data set that we obtained is limited, and we failed to reveal any regular trends.

EXPERIMENTAL

In synthesis of dtc_3Sm, we started from samarium metal and sodium diethyldithiocarbamate (pure grade). By reaction of samarium with the corresponding acids we prepared $SmCl_3$ and $Sm(NO_3)_3$.

Samarium diethyldithiocarbamate (aqueous solution). A 0.8 M solution of $SmCl_3$ or $Sm(NO_3)_3$ in distilled water was added to a 0.8 M solution of dtcNa in distilled water. The mixture was stirred for several minutes. The precipitate was allowed to settle, after which it was filtered off, washed with distilled water to remove NaCl, and dried in air at 60–80°C.

Samarium diethyldithiocarbamate (nonaqueous solution) was prepared from solutions of sodium diethyldithiocarbamate and samarium trichloride in ethanol. All manipulations were performed under argon. The starting $SmCl_3$ was dried according to [10]. Sodium diethyldithiocarbamate trihydrate was dehydrated in a vacuum at room temperature. Acetonitrile was distilled from P_2O_5. Ethanol was dehydrated. To a solution of 10.1 g of dtcNa in absolute ethanol, we added a suspension of 4.98 g of $SmCl_3$ in absolute ethanol. The mixture was stirred for several minutes. After that, the solvent was removed and replaced by acetonitrile. The precipitate of NaCl and other products insoluble in acetonitrile was filtered off. As a result, dtc_3Sm was obtained; mp 175–180°C, yield 85%, decomposes at 370–375°C to form cubic SmS. IR spectrum, ν, cm^{-1}: 1475, 1300, 1208, 1135, 1000, 995, 990, 980, 915, 842. Found, %: C 30.00; H 5.00; N 7.00; S 32.00; Sm 24.9. $C_{15}H_{30}N_3S_6Sm$. Calculated, %: C 30.00; H 5.2; N 9.3; S 25.6; Sm 20.0.

The adduct $dtc_3Smbipy$ was prepared similarly to dtc_3Sm with addition of 3 g of 2,2'-bipyridine in absolute ethanol. After recrystallization from chloroform, a colorless crystalline compound was isolated; mp 235°C, yield 94%, decomposes at 390°C to form cubic SmS. IR spectrum, ν, cm^{-1}: 1590, 1480, 1300, 1208, 1135, 1005, 1000, 915, 842, 770, 640. Found, %: C 39.50; H 5.05; N 9.10; S 25.00; Sm 19.80. $C_{25}H_{38}N_5S_6Sm$. Calculated, %: C 39.96; H 5.10; N 9.32; S 25.61; Sm 20.01.

The complexes with phenanthroline were prepared similarly. After recrystallization from chloroform, a colorless crystalline compound was isolated; mp 220°C, yield 90%, decomposes at 390°C to form cubic SmS. IR spectrum, ν, cm^{-1}: 1480, 1297, 1208, 1135, 1000, 995, 990, 980, 915, 840. Found, %: C 41.50; H 5.20; N 9.00; S 24.00; Sm 19.00. $C_{27}H_{42} \cdot N_5S_6Sm$. Calculated, %: C 41.61; H 5.43; N 8.99; S 24.68; Sm 19.29.

The installation for film deposition consisted of a heater with a massive steel plate for temperature equalization, a quartz cylinder limiting the reaction zone, and a sprayer fixed in the center above the cylinder. The support was placed on the plate. Its temperature was controlled with a thermocouple. The glass sprayer has an orifice 100–200 μm in diameter for the liquid and a ring-shaped slit of 50–100 μm width for compressed air. At an air pressure of $(0.6–1.2) \times 10^5$ Pa, this device produces fine drops of the solution of the starting compound. The solvent completely volatilizes from these drops during transport to the support. As a result, in the vicinity of the support the precursor occurs as vapor mixed with air and with the solvent vapor. The reaction products are removed by the counterflow along the cylinder walls through its upper open part.

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