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Tin colloids and metal-metal oxide films prepared by chemical liquid deposition. III

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Abstract: Colloids and thin metal-metal oxide films have been prepared by a method we call Chemical Liquid Deposition (CLD). The metal is evaporated to yield atoms which are solvated at liquid nitrogen temperature, and upon warming stable liquid colloidal solutions are formed. In the case of tin, the particle size of these colloids ranges between 200–500 Å. Zeta potentials were calculated by a Hückel approximation for most of these negatively charged particles. Upon solvent removal, colloidal particles coalesce to form films, which contain some residual solvent. The synthesis of colloids and films from Sn with acetone, 2-butanone, THF, ethanol, 2-propanol, DMF and DMSO is reported. FTIR, High Resolution Mass Spectrometry, Thermogravimetric Analyses (TGA) and Scanning Electron Microscopy (SEM) film characterization has been carried out. These studies indicate that solvents are incorporated into the films. The resistivity studies showed that they more behave as semiconductors than pure metals. TGA studies reveal that loss of weight occurs within 200–500 °C. The films are very stable with 5–10% weight loss at 550 °C. SEM reveals their surface morphology. Mössbauer gives information about oxidation states of some tin films.

Key words: Metal colloids – metal particles – films – chemical liquid deposition – semiconductors

Introduction

The cocondensation of metal atoms with organic solvents at 77 K produces several interesting reactions [1]. Of recent interest have been solvated metal atoms [2], in whose solutions the atoms are only "lightly stabilized". This solvation has proven to be a useful route to metal colloids that are very stable at room temperature [3, 4].

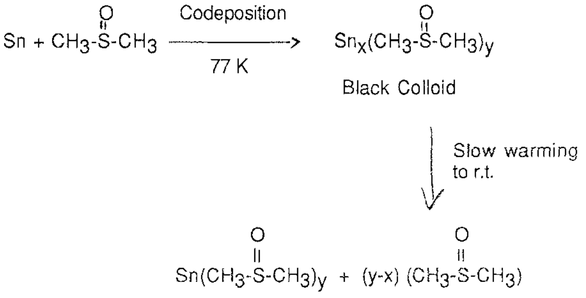
Although aqueous metal colloids are well known [5] and have been commercially used for centuries [6], non-aqueous systems have been obtained only recently [7], probably due to the absence of effective synthetic methods. The more successful approach for the preparation of stable metal colloids in organic solvents is based on the clustering of metal atoms at low temperature [8].

This new method is open to many metals or solvents and the resultant colloidal particles are free of interferences and impurities generally present in aqueous preparations.

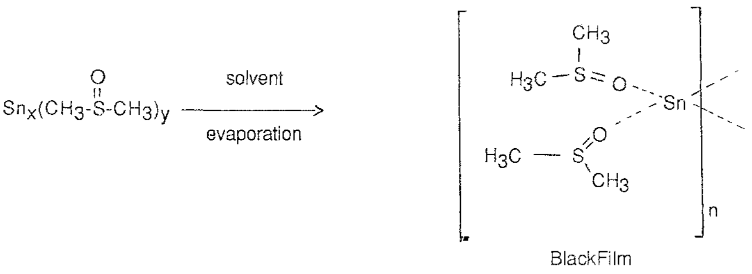
The solvated metal atoms are interesting from another point of view. When the solvate decomposes, the atoms begin to cluster in the organic medium. This clustering is affected by the organic solvents, the metal, concentration, and temperature. Colloids, powders, supported catalysts, or films may result.

The stabilization of colloidal particles can be explained by two mechanisms: i) steric, by solvent ligation, and ii) electrostatic; colloidal particles are charged due to adsorption of ions generated in the solution [9].

Another feature of these new colloidal systems is their tendency to form films upon solvent removal [10–12] (Scheme 1). They can grow to films under mild conditions. These new materials may have unusual optical, magnetic and



Scheme 1. Tin colloid formation



Scheme 2. Tin thin film formation

electrical properties. Scheme 2 shows the film formation.

Experimental

Preparation of Sn-DMF colloid

The metal atom reactor used (3L) has been described in previous reports [12, 13]. As an example, an alumina-tungsten crucible was charged with 0.4 g Sn metal. DMF (200 g) just distilled and dried was placed in a ligand inlet tube and freeze-pump-thaw degassed with five cycles. The reactor was pumped to 1×10^{-4} Torr while the crucible was warmed to red heat. A liquid nitrogen filled Dewar was placed around the vessel and Sn (0.068 g) and DMF (90.2 g) were codeposited over a 1-h period. The matrix was a black color at the end of the codeposition. The matrix was allowed to warm for 1.5 h to r.t. slowly under vacuum by removal of the liquid nitrogen Dewar. Upon meltdown, a black dispersion was obtained. After addition of nitrogen, up to 1 atm, the dispersion was allowed to warm for another 0.5 h to room temperature. The solution was siphoned out under nitrogen into a flask. Based on metal evaporated and DMF consumed, the molarity in metal could be calculated.

Scanning electron microscopy studies (SEM)

Electron micrographs were obtained on a ETEC Autoscan U-1 Model and the films were coated with gold for 3 min to obtain a 150 Å thickness using an Edwards S 150 Sputter coater.

FABS chemical ionization mass spectrometry (CIMS) of Sn-films

The CI/NH_3 mass spectra of films were obtained at different mVolts. The experiments were carried out with use of a VG Analytical 7070-HF, high resolution, double focusing mass spectrometer equipped with a VG 11/250 data system.

Thermogravimetric analysis

The thermogravimetric data were obtained using a Thermobalance TGS-1 Perkin Elmer with 2–5 mg samples heated under nitrogen flow (50 ml min^{-1}) at 10 °C min^{-1} from 25° to 550 °C.

Elemental analysis

The samples for microanalysis were handled by our Department of Chemistry (Microanalysis Laboratories). The metal samples were determined by atomic absorption after previous acid treatment. On the other hand, C, H, N, or S were determined by using a standard automatic analyzer.

Infrared Spectra (FTIR)

Infrared spectra were obtained using a Bruker IFS-25 Fourier Transform Infrared Spectrometer. KBr pellets were prepared for all the films. Spectra were recorded at a resolution of 2 cm^{-1}. Sixty-four scans were accumulated for each spectrum.

Solubility studies

The films were completely insoluble in several solvents: acetone, ethanol, 2-butanone, 2-propanol, THF, DMSO, toluene and *n*-pentane. The films were tested for 24 h of contact under stirring at 25 °C.

Conductivity

A Keithley Power Supply Model 241 and an Electrometer Keithley Model 610C were used to measure conductivity. The metal covering was achieved by using an Edward High Vacuum Ltd. Coating Unit Model 12EA 1650.

Results and discussion

A series of black colloidal solutions using different solvents was prepared and the results are summarized in Table 1. In order to learn more about the metal particles, several measurements were carried out.

Colloidal tin particle studies

Electrophoresis: Most of the previously reported aqueous metallic colloidal particles carried some negative charge [9], and the rate of migration of these particles to a positive pole can be determined as the electrophoretic mobility ($\mu\varepsilon$). For most of the colloids the velocity of migration was determined (see Table 1). These values are similar to those obtained for Pd-acetone colloids [8]. The $\mu\varepsilon$ values are similar to those reported for a variety of aqueous colloidal particles, e.g., colloidal gold, $30\text{–}40 \times 10^{-5}$ ($>$ 100 nm particle diameter), colloidal lead, 12×10^{-5} ($>$ 100 nm) [5a, 16].

The Debye–Hückel approximation may be used to express the charge density as a function of potential if it is low [14]. The ζ (zeta) potential can be calculated according to the convention of Hunter [15] and the Hückel equation. The ζ values are very large compared with those reported for Pd-acetone and/or for several aqueous sols, i.e., 18–58 mV [5a]. There are not many data available for non aqueous solvents. The data are summarized in Table 1.

Flocculation

Various electrolytes were added to the Sn-colloidal sols in order to induce flocculation [9]. Three solutions, 0.01 M of NaI, CaI_2, and $AlBr_3$ were prepared in acetone, respectively.

Addition of NaI solution to a 0.0013 M Sn-acetone colloid in Na:Sn ratio of 1:1 caused flocculation to begin in 2.5 h at room temperature. Addition of CaI_2 solution to the colloid in the same ratio caused flocculation to begin in 1.0 h. Finally, an addition of $AlBr_3$ solution to the colloid in the same M:Sn ratio induced flocculation immediately. Results are in agreement with data reported by Furlong [17] in which high-valent cations induced flocculation faster than

Table 1. Particle size, charge, and zeta potentials of Sn colloids

Colloid	Conc. × 10^3 M	Size (Å)	Velocity migration (mm/h)	Zeta potential (mV)*	Stability (h)
Sn-acetone	17.4	280	7.75	1076	48
Sn-2-butanone	15.9	250	—	—	72
Sn-THF	14.8	318	3.50	1.9	72
Sn-ethanol	21.4	400	2.15	890	120
Sn-2-propanol	9.9	300	—	—	144
Sn-DMF	6.2	500	3.00	5918	∞
Sn-DMSO	28.8	208	3.25	12437	∞

All the colloids are negatively charged

monovalent cations. Addition of water to the colloid induced flocculation only after 120 h at room temperature.

pH measurements

No evidence for increased acidity or basicity was obtained by measuring the pH of the colloidal solutions. Similar values for pure solvents and colloids were observed for acetone, 2-butanone, ethanol, and DMF.

Stability

The more stable colloids occur in DMF and DMSO but 2-propanol and ethanol are also very effective and enabled colloid stabilization for 6 and 5 days, respectively (see Table 1). However, the least stable colloid was Sn-acetone (2 days at r.t.) which is contrary to findings with Pd-acetone (stable for several months). For alcohols the stability decreases with increase in the hydrocarbon chain. The stabilities of the colloids correlate well with the dielectric constant (*D*) of the solvents (DMSO and DMF have the highest *D* and furthermore, ethanol and 2-propanol have the lowest values).

On the other hand, for ketones, due to their similar D, the difference appears to be due to their viscosities. However, if we compare stabilities reported before [19], the Au and Pd colloids are in general more stable. Thus, as might be expected, the metal involved is of great importance [20].

Elemental analysis

The Sn films were obtained after vacuum evaporation of solvent over a period of several hours at 10^{-3} Torr. In spite of this, substantial amounts of carbon and hydrogen remained attached to the films (see Table 2). Most of the films exhibited a C/H ratio between 2.0 and 3.0. It is also interesting to note the presence of N and S in DMF and DMSO films, respectively.

SEM and TEM studies

Dilute solutions were dripped on carbon coated copper grids in such a way that solvent evaporation left particles. Our TEM micrograph (Fig. 1) showed spherical particles ranging from 150–500 Å (see Table 1).

Table 2. Composition of thin films

Solvent	Concn, M ($\times 10^3$)	%Sn[a]	%C	%H[b]
Acetone	17.4	92.4	4.09	1.23
2-Butanone	15.9	90.9	5.45	1.63
THF	14.8	94.3	3.30	1.57
Ethanol	21.4	96.3	1.68	0.51
2-Propanol	9.9	75.2	6.92	1.27
DMF[c]	6.2	92.9	4.11	1.91 (0.51)
DMSO[d]	28.8	86.5	4.83	2.05 (5.15)
Benzene*)	10.0	89.0	2.20	0.93
Toluene*	15.6	68.4	1.79	0.02

[a] Microanalyses were obtained from Facultad de Ciencias Quimicas, Universidad de Concepcion

[b] Oxygen is the most likely missing percentage

[c] In parentheses nitrogen content

[d] In parentheses sulphur content

*) These films come from a non-colloid; the sols were metal dispersed in the solvent

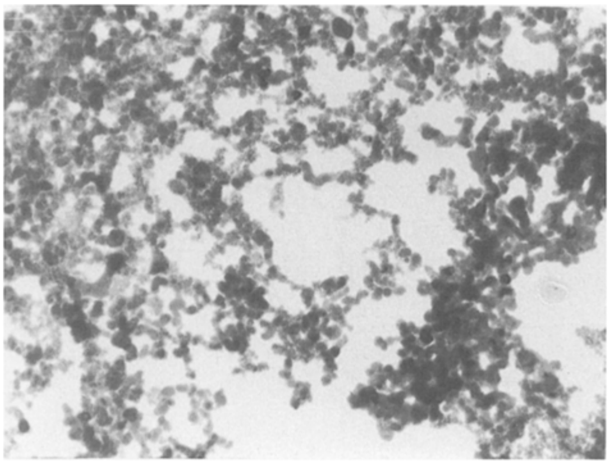


Fig. 1 TEM micrograph of Sn-2-butanone at $2.2 \times 10^4 \times$

Scanning electron microscopy showed that the films formed by solvent evaporation are made up of irregular surfaces such as with Sn-DMF and Sn-THF. This morphology can be seen in Fig. 2. However, Sn-acetone exhibits a more regular surface and we were able to obtain some electrical conductivity values (see Table 3).

Films of different thickness (1–10 nm) were prepared by dripping the colloidal solutions on a glass plate. Only the films with homogeneous surfaces exhibited semiconductor behavior. Due to ease of oxidation of the Sn films, the conductivity values summarized in Table 3 are in fact due to

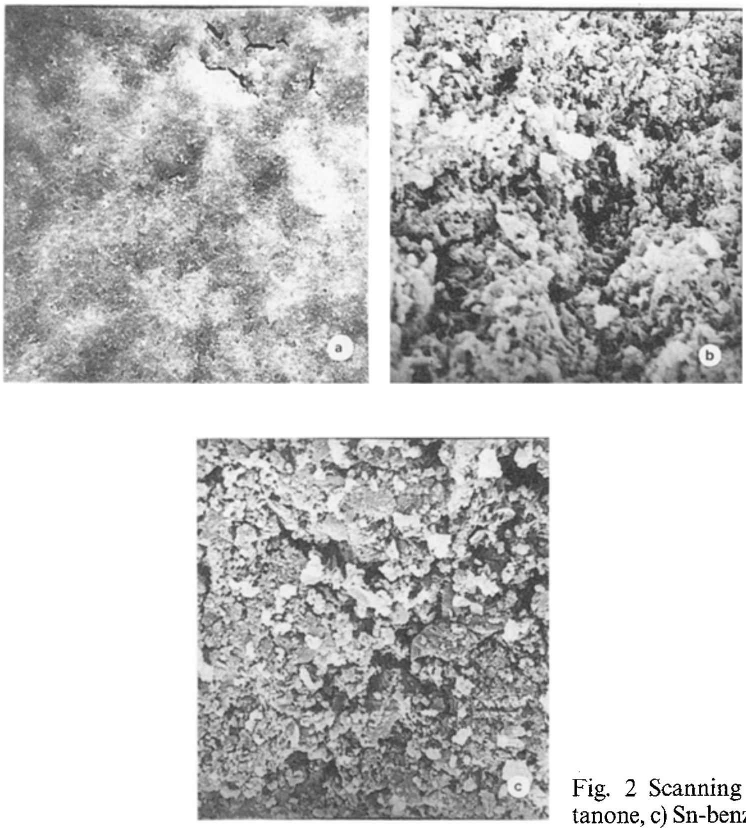


Fig. 2 Scanning electron micrograph. a) Sn-DMF, b) Sn-2-butanone, c) Sn-benzene, at 4000 magnification, 2.2×10^4 magnification.

Table 3. Conductivity

Sample	Wide (cm)	Long (cm)	Thickness (nm)	Resist. (Ω)	*V*. max.	*I*.max.	Conduct. $(\Omega\text{-cm})^{-1}$
Sn-acetone	0.5	1.0	1–10	*)	16	11*)E – 3	13.75
Sn-2-butanone	1.0	1.5	1–10	*)	800	4.4*)E – 3	8.0*E – 3
Sn-ethanol	—	—	—	—	—	—	—
Sn-2-propanol	0.55	1.3	1–10	*)	*)	*)	3.8E – 2
Sn-THF	—	—	—	—	—	—	—
Sn-DMSO	1.1	1.1	1–10	*)	*)	*)	343
Sn-DMF	*)	*)	*)	54	*)	*)	28
Sn-toluene	—	—	—	—	—	—	—
Sn-benzene*)	—	—	—	—	—	—	—
Sn**)							

— Unknown due to bad contacts
*) Irreproducible values
**) A film was prepared by direct evaporation of the metal under vacuum on a glass cover

a mixture of Sn, SnO, and SnO_2 with the corresponding solvents.

FTIR

Infrared spectra of films derived from Sn-acetone showed bands at 2950 cm^{-1} (v_{C-H}), 1260 1100 cm^{-1} ($v_{C=O}$). The disappearance of $v_{C=O}$ might indicate a metal bonded to the ketone through a Sn–O bond. Sn-2-butanone also exhibited bands at 2950 and 1255 cm^{-1}. Sn-propanol presented bands at 2950 cm^{-1} and 660 cm^{-1}. Sn-DMF showed bands at 2820 cm^{-1}, 1640 cm^{-1} $v_{C=O}$ and N–H deformation) and 670 cm^{-1}

(amide band). Finally, Sn-THF showed bands at 2950 cm^{-1} 1275, 1640, and 670 cm^{-1}. Apparently, the ketones in the films are bonded through a metal-oxygen bond and for this reason the $v_{C=O}$ disappears.

Thermal stabilities

Most of the films are very stable and lose only around 5% of their total weight. Only Sn-benzene and toluene, which were not colloids, exhibit a greater weight loss. In Table 4 are summarized the data from thermograms of these Sn derived films.

Sn-DMF is the more thermally stable film (463–553 °C), followed by Sn-2-propanol (433–493 °C). This last value is very similar to that of Ge-2-propanol reported before [21]. The stabilities of Sn-ethanol and Sn-2-butanone are less than 413 °C.

Sn-acetone and Sn-THF are the least stable and decompose at 393–493 °C. In most of the cases, the increase in the hydrocarbon chain length increases the stability of the films. The total weight loss is very low for Sn-ethanol, Sn-2-propanol, and Sn-acetone, with a range between 1–2%.

Mass spectrometry (FABS)

The films were analyzed as follows. Sn-2-propanol was studied at $l = 538$ mVS. The spectrum showed peaks at *m/z* 224, 182, 178, 164, 127, and 103. The *m/z* signal at 224 is probably due to $[\mathrm{CH_3CHOHCH_3})_4]^+$ minus an oxygen atom and by a loss of 46 gives *m/z* 178. The loss of $\mathrm{CH_3CHOHCH_3}$ from the 224 species would give 164.

Sn-DMF was studied at $l = 2.0$ mVS. The spectrum showed peaks at *m/z* 146, 131, 116, and 104. The *m/z* 146 peak corresponds to the dimer $(\mathrm{HCO{-}N(CH_3)_2})_2$ by losing formaldehyde $(\mathrm{M}\text{-}30)^+$ to give *m/z* 116. Also, *m/z* 104 can be formed by losing $\mathrm{N{=}C{=}O}^+$ from the original fragment. The M-15 gives the peak *m/z* 131.

Sn-DMSO was studied at $l = 222$ mVS. The spectrum showed peaks at *m/z* 227, 193, 179, 165, 138, 126, 112, and 100. In *m/z* 227 we can distinguish $[(\mathrm{CH_2SOCH_2})_3]^+$ minus H by the loss of $\mathrm{H_2S}$ we get *m/z* 193. Successive loss of $\mathrm{CH_2}$ gives 179 and 165.

Sn-2-butanol was studied at $l = 499$ mVS. The spectrum showed peaks at *m/z* 221, 203, 192, 175, 139, 125, 111. The *m/z* 221 peak corresponds to $[(\mathrm{CH_3CHOHCH_2CH_3})_3\text{–}\mathrm{H}]^+$ minus H, by losing COH to give *m/z* 192. From the original fragment loss of water gives *m/z* 203. The loss of $\mathrm{C_2H_4^+}$ gives 175.

Sn-ethanol was studied at $l = 222$ mVS. The spectrum showed peaks at *m/z* 163, 151, 123, 109. The *m/z* 163 peak corresponds to $[(\mathrm{CH_3CH_2OH})_4]^+$ with loss of $\mathrm{H_2}$ and $\mathrm{H_2O}$. Further water loss gives *m/z* 123. The loss of $\mathrm{CH_2}$ gives *m/z* 109.

Sn-acetone was studied at $l = 173$ mVS. The spectrum showed peaks at *m/z* 137, 116, 111 and 102, which are probably due to fragments of acetone trimers with loss of COH or $\mathrm{CH_2}$ to give 116 and 102.

Table 4. Thermogravimetric analysis

Solvent	Concent. 1*E3 M	Temperature range °C	Initial wt. (mg)	Final wt. (mg)	Percentage loss %
Ethanol	21.4	413–453	1.22	1.20	1.35
2-Propanol	9.9	433–493	0.94	0.93	0.90
2-Butanone	7.3	—	—	—	—
2-Pentanol	9.1	—	—	—	—
Acetone	17.4	393–493	0.61	0.60	2.00
2-Butanone	15.9	413–483	2.22	2.18	2.00
THF	14.8	393–453	0.63	0.61	3.00
DMF	6.2	463–553	0.62	0.55	8.00
DMSO	28.8	403–553	4.28	3.76	12.6
Toluene (A)	15.6	433–523	3.25	2.76	15.0
Benzene (B)	10	428–493	1.30	1.20	3.85

A, B, are not colloid, metal dispersed in the solvent
— no measurements

Sn-THF was studied at $l = 1.8$ mVS. The spectrum showed peaks at m/z 316, 224, 207, 192, 158, 140, 125, 111. This is probably a mixture of fragmented telomers with loss of CH_2 and loss of water.

Mössbauer Spectra. In all the films, according to Isomer Shift (δ) and Quadrupole Splitting (Δ), most of the species are Sn^{4+} ($\delta = 0$–0.18 mm/s, $\Delta = 0.32$–0.90 mm/s), Sn^{2+} ($\delta = 2.80$–2.95 mm/s, $\Delta = 1.5$–2.11 mm/s) with a low content of Sn^0 ($\delta = 2.57$ mm/s) [22].

Conductivity

Most of the films were tested for semiconductor behavior. The conductivity was measured by direct reading of voltage and current on samples deposited on a glass surface. The electrical contact was made by metallic covering with copper under vacuum and/or using a silver paint spot. Only, Sn-DMF, Sn-DMSO and Sn-acetone films behaved as semiconductors if we compare them with pure metal (see Table III). This is probably due to the cracking of the film (Fig. 2) which prevents good measurements.

Conclusions

These films can be obtained on several surfaces such as glass, plastic, and metals by spraying the respective solutions on each. Also, it is possible to transfer the films to adhesive tape. One of the problems is to get good quality films, since the films are very reactive. Indeed, the Mössbauer indicates a mixture of Sn^{4+}, Sn^{2+} and Sn^0. Thus, our Chemical Liquid Deposition (CLD) method in the case of tin yields a Sn–SnO–SnO_2 mixed film.

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