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THIN METALLIC FILMS FROM SOLVATED METAL ATOMS(U) KANSAS 1/1

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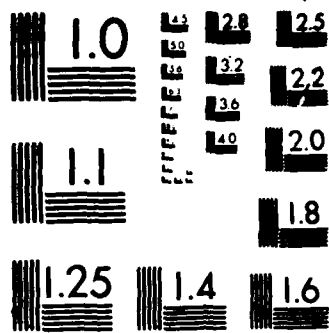
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Abstract

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Thin metallic films from solvated metal atoms*

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ABSTRACT

Metals were evaporated under vacuum and the metal atoms solvated by excess organic solvents at low temperature. Upon warming stable colloidal metal particles were formed by controlled metal atom clustering. The particles were stabilized toward flocculation by solvation and electrostatic effects. Upon solvent removal the colloidal particles grew to form thin films that were metallic in appearance, but showed higher resistivities than pure metallic films. Gold, palladium, platinum, and especially indium are discussed.

1. INTRODUCTION

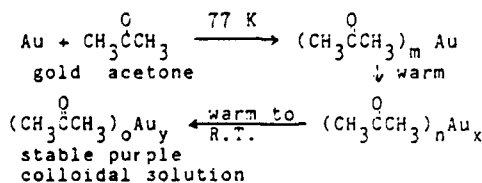
In the field of chemistry an active and broad area of research has developed over the past two decades that deals with the generation of atoms of metals (by metal evaporation) and the interaction of these free atoms with organic chemicals at low temperature.^{1,2} Many new organometallic compounds and catalysts have been synthesized this way, and new understanding of bonding in such substances has been gained. In order to carry out such experiments metal vapor synthesis (MVS) reactors have been devised that evaporate metals under vacuum by resistive heating, electron beams, or lasers. The metal vapor (atoms) is allowed to fly to a cold wall (10⁻³ - 77 K) where organic or inorganic chemicals (reactants) are being deposited and frozen. In this way metal atoms are immersed in an excess of reactant compound. Upon codeposition, or later warming of the matrix, chemical reactions take place. One important aspect of this work has been the combination of selected metals and reactants so that controlled metal atom reaggregation can be achieved, and colloidal dimension metal particles can be prepared.

2. COLLOIDAL METAL PARTICLES

Deposition of relatively unreactive metal atoms with relatively inert reactants (often solvents like toluene, acetone, tetrahydrofuran, etc.) leads to a situation where upon warming the matrix, metal atom reaggregation occurs to form metal dimers, trimers, and eventually clusters of hundreds of atoms. Thus, weakly solvated metal atoms yield weakly solvated metal particles, and in some cases these particles are colloidal size 1 - 1000 nm, and remain suspended indefinitely in the solvent at room temperature. These particles are stabilized toward further growth by solvation (steric effects) and by electrostatic effects (charging of the particles). However, this stabilization can be overcome by solvent removal, and further particle growth eventually yielding metal films under mild conditions can be achieved. Thus, the particles are living in the sense that further growth can be stimulated by solvent removal.

3. GOLD

Although aqueous colloidal gold, from reduction of gold salts, has been known and used medicinally for centuries,^{3,4} it has been difficult to prepare colloidal gold in non-aqueous media. Thus, our preparation of colloidal gold from solvated metal atoms has added a new dimension.^{5,6} Particle size can



be controlled by dilution effects, and by warming rate. Stabilization of the particles is due to solvation effects and electrostatic effects. Electrophoresis studies showed that

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the gold particles were negatively charged, apparently due to electron scavenging from the solvent medium. Particle sizes according to TEM studies ranged from 2 - 9 nm depending on exact preparative procedure. However, photon correlation spectroscopy (PCS) indicated 200-600 nm, and plasmon absorption spectroscopy indicated 65 - 75 nm, which suggests that weak particle agglomeration occurs in solution. TEM also shows evidence for such loose particle agglomeration, and chains of spherical particles were often observed.

Since this method of preparation does not involve chemical reduction of gold salts, the colloidal solutions are free of interfering byproducts (chloride ion, etc.). We find that this pure form of the colloidal particles allows their further growth to films. We have found that gold films can be prepared either by dripping the colloidal solution on a glass plate (or other substrate) and allowing the solvent to evaporate, or by spraying the colloidal solution out of a spray atomizer. Films of various thicknesses were prepared: 20 nm was non-conductive and light purple in color; 120 nm, non-conductive, slight metallic appearance mixed with purple coloration; 4500 nm, metallic appearance, resistivity = 1.8×10^{-2} ($\Omega\text{-cm}$). This can be compared with bulk gold where $\rho = 2.4 \times 10^{-6}$.

4. PALLADIUM AND PLATINUM

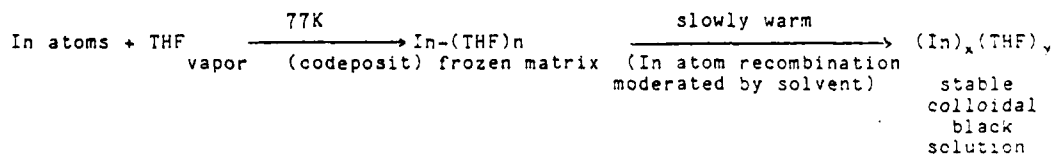
Black colloidal solutions were formed and stable in acetone, ethanol, isopropyl alcohol, and tetrahydrofuran.⁷ Electrophoresis studies indicated that the particles were negatively charged, and thus stabilized by electrostatic effects as well as solvation effects. Films of palladium were prepared by solvent removal, and they appeared metallic. However, the dry films contained about 2% residual solvent that could be displaced by other solvents. Overall the dry films contained about 5% carbon, 0.5% hydrogen, and 10 - 15% oxygen by weight. Due to this residual carbonaceous material the resistivities of the films were higher than for pure palladium. 50,000 nm thickness, $\rho = 4 \times 10^{-2}$ ($\Omega\text{-cm}$) after heating to 140°C, $\rho = 2 \times 10^{-2}$ ($\Omega\text{-cm}$); these can be compared to a pure palladium film $\rho = 0.1 \times 10^{-2}$ and bulk palladium $\rho = 11 \times 10^{-6}$.

5. INDIUM

Indium oxides, hydroxides, and phosphates in the form of colloidal particles have been found to be useful in medicine.⁸⁻¹⁵ For example ^{113m}In labeled phosphate colloids are very effective for liver and spleen scanning.¹² The short half-life of ^{113m}In minimizes some side effects of such radiation treatment.¹³ Indium metal and indium oxide films are also important, particularly as semiconductors.¹⁶⁻²³ Thus, indium oxide films are being used in solar energy conversion devices. These films are n-type degenerate semiconductors with a band gap of 2.6 - 3.7 eV.¹⁸ Due to their relatively high conductivity and high transparency in the visible part of the solar spectrum, these films are also used as transparent contacts for solar cells.²¹

What we report here are the first examples of non-aqueous indium colloids, their film forming properties, and oxidative conversion to indium oxide films.

a. Colloidal Solutions The following scheme was used to prepare In-colloidal solutions using tetrahydrofuran (THF) as a typical solvent.^{1,24}



The colloidal solutions prepared in this way were black in color. A variety of solvents were used successfully: ethanol, isopropanol, isopropanol-acetone, acetone, 2-butanone, THF, dimethyl formamide (DMF), toluene, dimethyl sulfoxide (DMSO), and water. Varying degrees of stability toward flocculation were observed, as shown in Table 1. Generally about 0.1 g In was suspended in 100-200 ml solvent. Several approaches to characterization of the indium particles are now described.

Electrophoresis-Generally aqueous metal colloid particles carry some negative charge,²⁵⁻²⁷ and the rate of migration of these particles to a positive electrode can be

Table 1. - Stability and Size of Indium Colloids

Solvents	[M] range	Stability (hours)	Color	Film Forming?	Size(nm)
Ethanol	0.0123	0.5	black	yes	6
Isopropanol	0.0115-0.0307	72	black	yes	7
Isopropanol-Acetone	0.0214	2	black	yes	4
Acetone	0.0696-0.030	1	black	yes	4
2-Butanone	0.030	1	black	yes	8
THF	0.0075-0.078	96	black	yes	20
DMF	0.095-0.0162	30	black	yes	25
Benzene	0.0063	0	black	no	-
Toluene	0.0084-0.0085		black	yes	-
DMSO	0.0191	∞	brown	yes	8
H ₂ O	0.0147	1	black	no	-

determined, which is the electrophoretic mobility. With our most stable colloids, namely In-THF and In-isopropanol, we were able to carry out these experiments. In our 0.0075M In-THF solutions (indium particle size 20nm), the rate of migration was found to be 10mm/h. For a 0.0307M In-isopropanol solution this rate was 9 mm/h. From these values electrophoretic mobilities μ_E can be calculated.

In-isopropanol (0.0307 M in indium)

$$\text{Field Strength} = X = \frac{E}{l} = \frac{-12.67V}{23.5cm} = -0.539V/cm$$

$$\text{Velocity} = V = \frac{9.0mm}{3600s} = 2.5 \times 10^{-3} \text{ mm/s}$$

$$= 2.5 \times 10^{-4} \text{ cm/s (for 7 nm particles)}$$

$$\mu_E = \frac{V}{X} = \frac{2.5 \times 10^{-4} \text{ cm/s}}{-0.539 \text{ V/cm}} = -4.6 \times 10^{-4} \text{ cm}^2/V.s.$$

$$= -4.6 \times 10^{-8} \text{ m}^2/V.s$$

This value for μ_E is similar to those reported for a variety of aqueous colloidal particles, eg. colloidal gold = $3-4 \times 10^{-4} \text{ cm}^2/V\text{-sec}$ (< 100 nm particle diameter), colloidal platinum 2×10^{-4} (< 100nm), colloidal lead 1.2×10^{-4} (100 nm), and oil droplets = 3.2×10^{-4} (2000 nm).^{26,27}

The Debye-Huckel approximation may be used to express the charge density as a function of potential if it is low.²⁸ The potential at the surface of the particle is defined as the zeta potential ζ . The zeta potential can be calculated according to the convention of Hunter²⁹ and the Huckel equation:

$$\mu_E = 4\pi E_0 D \zeta / 6\pi \eta = 2E_0 D \zeta / 3\eta$$

where for isopropanol

$$D = \text{dielectric constant} = 18.3$$

$$E_0 = \text{permittivity (vacuum)} = 8.854 \times 10^{-12} \text{ F/m}$$

$$\eta = \text{solvent viscosity} = 1.375 \times 10^{-3} \text{ N-s/m}^2$$

$$\mu_E = \left(\frac{2}{3}\right) (8.854 \times 10^{-12}) (18.3) \ell / 1.375 \times 10^{-3}$$

$$\ell = 1.27 \times 10^7 \mu E$$

$$\ell = (1.27 \times 10^7)(-4.6 \times 10^{-6})$$

$$\xi = -580 \text{ m volts}$$

This value is very high compared with a variety of aqueous sols, i.e. -18 to -58 millivolts,²⁶ and compared with our recent report on Pd colloids in acetone (-44 millivolts).⁷ It reflects a relatively high μ_E coupled with a solvent of high viscosity. Thus, we can conclude that the indium particles possess a relatively high negative charge.

It seems clear that the In particles scavenge electrons from the solvent and reactor environment. Collections of solvent molecules probably serve as the counter ions setting up the diffuse double layer (which is broken down during the electrophoresis experiment). As with Au and Pd,^{5,7} this charge accumulation on In particles serves as an electronic mode of colloid stabilization. This, coupled with solvation, a form of steric stabilization, allows good stability toward flocculation.

Flocculation and Particle Sizes Black colloidal solutions could be prepared in a wide variety of solvents, as shown in Table 1. Generally the more polar organic solvents yielded colloidal particles most stable toward flocculation at room temperature. In particular dimethylsulfoxide (DMSO), isopropanol, and tetrahydrofuran (THF) were best in this regard.

Interestingly, particle size varied with solvent (Table 1). Acetone yielded the smallest particles (4 nm) while THF and dimethylformamide yielded the largest (20-25 nm).

In our system, where dilute solutions of solvated atoms are allowed to migrate and cluster together, the final particle size depends on several factors: (1) strength of solvation of atoms vs growing clusters, (2) ease of desolvation during particle-atom encounters, and (3) rate of electron scavaging to yield electronically stabilized particles. We have found that particle sizes can be controlled by choice of solvent, or by solvent dilution. With indium, a rather reactive, oxidatively unstable metal, solvent choice is quite important. Chemical reactions with the solvent (in addition to solvation/ligation) can be important (evidence for different modes of interaction is found in the chemical analyses of films (see later)). We might conclude from these data that more strongly interacting solvents (eg., acetone) do not allow desolvation and particle growth as easily as more weakly interacting solvents (eg., THF). A better understanding of these growth - stabilization processes must await kinetic analyses of particle growth and behavior.

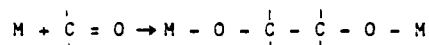
Oxidative Instability The method of aggregation of atoms of In at low temperature in an organic solvent leads to a colloidal solution of particles which possess a large surface area and relatively large surface atoms/bulk atoms ratio. And since In metal is very oxophilic, we would expect these solutions to be sensitive to oxygen. Indeed, they are. An In-isopropanol solution reacted vigorously with air. In fact rapid exposure can lead to explosive oxidation and, of course, concomitant combustion of the excess isopropanol.

Although this oxidative instability causes a serious handling problem, the In particles can be slowly, controllably oxidized to indium oxide particles and films.

b. Thin Films Similar to the behavior of gold and palladium, evaporation of excess solvent in the absence of oxygen leads to indium films containing some organic residue from the solvent.

Microanalyses of Films: Table 2 summarizes a number of elemental analyses of these dry films. All manipulations were carried out in the absence of oxygen to the best of our ability, (however, some adventitious oxygen is always a problem). Note the M,C,H analysis for In-ethanol and the average of several determinations for In-isopropanol. It is clear that substantial amounts of organic solvent remain coordinated and trapped within the In film and ratios of M:C are generally 2:1. Upon exposure of the In film to oxygen a vigorous reaction took place, which of course can be controlled by rate of oxygen exposure. The film residue after oxidation shows a greatly enhanced M:C ratio (now 3:1) and larger oxygen content as expected after the conversion of indium to indium oxide. Another interesting feature is that when ketones were used as solvents, much greater

amounts of organic material were incorporated into the films. This suggests that a chemical reaction took place, probably a ketone coupling, a reaction known to take place with reducing metals and carbonyl compounds:



No pure coordination compounds were formed, but colloidal particles with higher contents of organics and smaller particle size resulted. Other unsaturated solvents such as DMSO behaved similarly.

IR Analyses of Films: IR absorptions due to solvent molecules were easily observed. For example, In-isopropanol films showed bands at 3400, 2980, and 1020 cm^{-1} which can be assigned to OH, CH, and C-C. However, In-O bands at near 200 cm^{-1} ³⁰ could not be detected.

Resistivity of Films: The In-solvent films were converted to mainly indium oxide films by slow air exposure. Then resistivities were measured. Only the In-THF (oxidized) could be measured showing the thickness = 12,000 nm and $\rho = 130$ compared with $\rho = 8 \times 10^{-3}$ for bulk indium. All the rest showed infinite resistivity under the conditions of our experiments. Thus, it seems clear that the films, which are smooth in appearance under the microscope, are exhibiting high electrical resistance, probably due to micro-cracks in the film and/or incorporation of organic residues.

Electron Microscope Studies: Colloidal solutions were dripped onto carbon coated copper grids so that rapid solvent evaporation left isolated particles. According to TEM the particles were spherical and readily aggregated together, which is probably an artifact of the sample preparation procedure (as solvent evaporates the particles quickly aggregate). This aggregation was more severe in these studies compared with our earlier studies of Au and Pd systems. Particle sizes were estimated from the size of individual aggregated particles.

Scanning electron microscopy showed signs of film defects and the presence of small aggregates not yet incorporated fully into the film structure (Figs. 1 and 2). Heating of the film showed a smoothing effect (Fig. 3).

Table 2. Elemental Analyses of Indium Thin Films^a

Solvent	[M] solution	%In	%C	%H	Ratio(M:C:H:O:Y)
Ethanol	0.0123	73.45	3.63	1.33	2 : 1 : 4 : 4
Isopropanol	0.0115-0.0307	69.26	3.18	1.39	2 : 1 : 5 : 6
Isopropanol ^b	0.0094	77.15	1.03	0.31	8 : 1 : 4 : 17
Isopropanol-Acetone	0.0214	54.21	11.43	3.80	1 : 2 : 8 : 17
Acetone	0.069-0.030	60.08	8.64	2.68	2 : 3 : 10 : 7
2-Butanone	0.033	49.21	17.69	4.72	1 : 3 : 11 : 4
THF	0.0075-0.058	62.28	3.96	1.84	2 : 1 : 5 : 6
DMF ^c	0.0095-0.0162	60.97	3.77	1.51(0.33)	26:15 : 75 : 10 : 1
DMSO ^d	0.0191	60.15	8.36	1.95(5.13)	3 : 5 : 12 : 9 : 1

a The microanalyses were carried out by handling the films under N_2 to avoid oxidation. (Galbraith Laboratories).

b Film recently prepared and exposed to air. Analysis of the residue.

c In brackets, nitrogen microanalysis

d In brackets, sulfur microanalysis

c. EXPERIMENTAL SECTION: Preparation of a typical In-Acetone Colloid The metal atom reactor used in codeposition has been described previously.²⁴ As a typical example, a W-Al₂O₃ crucible was loaded with 0.5 g In metal.

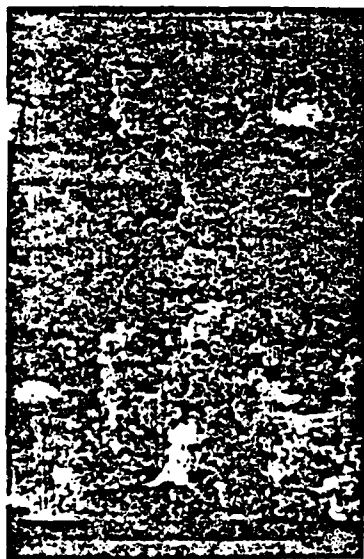


Figure 1 SEM micrograph of In-THF film



Figure 2 After heating In-THF film to 140°C



Figure 3 Thickness determination of In-THF film

Solvents (100-200 ml), previously dried were placed in the ligand inlet apparatus and freeze-pump-thaw degassed with several cycles. The reactor was pumped down to 1×10^{-4} Torr while the crucible was warmed to red heat. A liquid nitrogen filled Dewar was placed around the vessel and In (0.1 g) and THF (190 ml) were codeposited over a 1.5 h period. The matrix was brown-red in color at the beginning of the codeposition and darker at the end. The matrix was allowed to warm slowly under vacuum by removal of the liquid nitrogen Dewar. (1.5 h). Upon meltdown a gray-black solution was obtained. After addition of nitrogen the solution was allowed to warm for another 0.5 h to room temperature. The solution was syphoned out under N₂ flow into Schlenk ware. Based on In evaporated and THF inlet the dispersion molarity could be calculated. Electrophoresis Experiments. The electrophoresis experiments were carried out by using a glass U-tube of 11.0 cm each with a stopcock on the base to connect a perpendicular glass tubing of 13 cm long and 35 cm height.³¹ Platinum electrodes were attached to the top of the U-tube and through a ground glass joint to the pole of a 12 V battery. The solvents were placed in the U-tube and then the colloid solution added slowly through the side tube. The migration rate was determined based upon the average of the displacement in each side of the U-tube. A typical experiment was carried out for a period of 3 h at 25 C.

SEM and TEM Studies Electron micrographs were obtained on a JEOL, TEMSCAN- 100 Cx11 Combined electron microscope operated at 2.5×10^5 magnification. The specimens for TEM were obtained by placing a drop of the colloid solution on a copper grid which was coated by a carbon film. Resistivity Studies Films of different thickness (12-50 μ) were prepared by dripping the colloidal solutions on a glass plate edged with silicon rubber

adhesive resin. The solvents were allowed to evaporate under vacuum to minimize oxidation processes. Resistivities were measured by scrapping the silicon rubber away from the edges of the film, which was then trimmed to rectangular shape (this was done in an air atmosphere). It was then connected to electrodes on each end by vapor depositing a film of copper. The resistance of each sample was measured with a Digital Multimeter KEITLEY 178 Model. The vapor depositions were carried out using a Metal Evaporator VEECO Model VS-90. Infra Red Studies. Infrared spectra were recorded in a Perkin Elmer PE-1330 infrared spectrometer. IR studies of the metal films were carried out using KBr pellets.

6. ACKNOWLEDGEMENTS

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