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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Solvated metal atoms were employed to produce non-aqueous colloidal solutions; these were useful in preparing thin metal films in liquid phase. Metal-metal bonded compounds were studied; synthesis from metal atoms.		

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**A. General Description of Research Carried Out**

Metals such as Pd, Pt, Cu, Ag, Ga, In, Ge, Sn, and Pb were evaporated under vacuum and the vapors (atoms) cocondensed at 77°K with excess organic solvents. In this way solvated metal atoms were produced. Upon warmup to room temperature metal atom agglomeration occurred in certain solvents to yield stable colloidal particles in solution. In many cases these were the first examples of non-aqueous colloids of these metals, and they are very novel in that they are free of contaminating reducing agents, halide ions, etc., and they are living colloids--by removal of solvent metallic films can be grown on various substrates under very mild conditions. Characterizing these colloidal particles and the films therefrom was an important part of this project. *metals-metal bonds. ALLOYS*

A second area was the synthesis of new metal-metal bonded compounds, eg.  $R_2Al-AlR_2$ , as possible new Chemical Vapor Deposition materials for thin film production. Unusual synthetic approaches, some involving metal vapors, were used. Compounds containing Al, Ga, In, and As were considered. The advantage of such materials, on the microscopic level, is that two metal atoms could be deposited at a time on a hot substrate target, thereby generating films of novel structure/stoichiometry (when mixed metals are being codeposited).

**B. Brief Description of Results**

Our colloid and surface work continued throughout the contract and we have reported on Au, Pd and In colloidal dispersions in organic solvents. These living colloids behave as film precursors. We spent much of the time working with the In system and have been able to prepare and characterize In colloidal particles in THF, DMF, isopropanol, acetone, and other organic


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solvents. Films of indium metal and indium oxide were prepared and studied. We also found that stable Au and Pd colloids could be prepared in liquid styrene, and this purple solution could be controllably polymerized to metal doped polystyrene. This was the first preparation of stable metal colloids such as these in a useful monomer medium. Unusual stabilization mechanisms for these colloidal particles are of interest:

(1) the particles appeared to scavenge electrons to become negatively charged, and (2) strong solvation processes must be important. Electrophoresis studies, electron microscopy, electrolytic additions, plasmon absorption spectroscopy, and conductivity studies were valuable in characterization of particles and films.

A second major emphasis was the attempted synthesis of Al-Al, Al-As, Ga-Ga, and Ga-As bonded organometallic compounds. We met with limited success. However, we further elucidated the chemistry of Al and Ga atoms, As<sub>2</sub> dimer. We have discovered a facile synthesis of R<sub>3</sub>Ga<sub>2</sub>X<sub>3</sub> which may be an important discovery since it would allow a better route to R<sub>3</sub>Ga compounds for CVD processes.

### C. Most Recent Findings

The dispersion of metal vapor into fluorocarbon solvents has been of interest in recent months. Metal atom clustering in cold fluorocarbon solvents occurred as in analogous hydrocarbon solvents. The fluorocarbons did not stabilize colloidal suspensions at room temperature, and metal powder precipitated. However, a very interesting phenomenon is that these fluorocarbon derived metal powder were "soluble" in organic solvents. A good example is gold powder derived from perfluoro-tri-n-butylamine. Upon extraction (or treatment of the filter cake) with acetone, red colloidal

suspensions were obtained. The gold particles "dissolved" in this way were smaller than those obtained directly from metal atoms dispersed in acetone. For example, fluorocarbon derived particles were 10-40Å, while acetone derived were 50-90Å. Furthermore, the particles retained fluorocarbon; that is, according to X-ray fluorescence they are true gold but their surfaces appear to be fluorocarbon coated, thus their strange molecular behavior (ability to be dissolved and small size).

#### D. A Listing of Technical Reports Submitted

1. S. T. Lin, M. T. Franklin, and K. J. Klabunde, "Non-Aqueous Colloidal Gold. Clustering of Metal Atoms in Organic Media, 12," Langmuir, 2, 259 (1986).
2. K. J. Klabunde, editor, "Thin Films From Free Atoms and Particles," Academic Press, Orlando (1985).
3. K. J. Klabunde, "Introduction to Free Atoms and Particles," Chapter in 2 above.
4. G. Nieman and K. J. Klabunde, "Clustering of Free Atoms and Particles: Polymerization and Film Growth," Chapter in 2 above.
5. M. Franklin and K. J. Klabunde, Sym. High Energy Processes in Organomet. Chem. K. Suslick, editor, ACS Sym. No. 333, pg. 246 (1987).
6. G. Cardenas-Trivino, K. J. Klabunde, and B. Dale, Langmuir, 3, 986 (1987).
7. G. Cardenas-Trivino, K. J. Klabunde, and B. Dale, "Thin Metallic Films from Solvated Metal Atoms" Proceedings of SPIE, Vol. 821, 206 (1987).

8. K. Starowieyski and K. J. Klabunde, "Reactions of Vapors of Some Metals and Metal Oxides with Organometallics of Main Group Elements." App. Organomet. Chem., in press.

#### E. Importance of Past ONR Supported Work

The major contributions have been the discovery that colloidal metal particles can be prepared by agglomeration of solvated metal atoms, exploring part of the scope of this process, learning about particle stabilization mechanisms, and demonstrating that metal films can be prepared from these colloidal solutions. This work has opened up a new dimension in colloid chemistry and potentially in thin film production.

Two of our papers (1 and 5 above) discuss the history of colloidal metal particles and emphasize the novelty of our discovery. As a partial reiteration of the reasons such colloidal solutions are unique: (1) they are non-aqueous, (2) no metal salts reducing process is used so no byproducts are present as impurities, (3) the metal particles are "living" in the sense that simply by solvent removal particle growth occurs until films result, (4) films can be deposited on irregularly shaped objects, (5) the method allows particle deposition in polymer matrices, and (6) particle size can be controlled by metal: solvent ratios, solvent choice, and warm-up procedures.

Industrial interest in these colloidal solutions as film precursors has been extremely gratifying. Shortly after announcing our findings (after filing for patent protection), a series of events took place: a major company expressed their intent to license the patent and is paying the patent fees (the P.I. is a consultant for this company); the findings were summarized in three research and development magazines; the P.I. was

invited to speak at an international meeting of optical engineers (SPIE meeting in San Diego); reprint requests have been numerous; phone calls and letters from numerous industrial firms requesting more information and samples were received (the names of these firms can be provided on a confidential basis).

The firms interested in this technology invariably wanted to know if we could produce films on irregularly shaped objects such as metal parts, screens, and fabrics. Often such substrates cannot be coated by conventional vacuum evaporation/deposition methods. Another general theme was the need to deposit metal particles on or in composite materials or organic polymers. These and other interactions convince us that the work we are doing is certain to be useful to many high technology companies.

(These same scientists have expressed considerable general interest in a book the P.I. edited on "Thin Films from Free Atoms and Particles.")

**F. Personnel Involved**

Galo Cardenas-Trivino (postdoctoral, now on faculty at U. of Concepcion, Chile)

Ellis Zuckerman (postdoctoral)

K. Starowieski (visiting professor)

M.T. Franklin (M. S. student)

S.T. Lin (postdoctoral)

George Nieman (visiting professor)

B. Dale (collaborating physicist)