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GAS JET DEPOSITION OF MULTICOMPONENT ULTRAFINE MICROSTRUCTURES

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Block 20

ABSTRACT

The potential technological importance of multicomponent ultrafine microstructures makes it essential to develop methods of formation which permit both higher growth rates and improved control over material properties. During the course of our Phase I research effort, we have shown that our new proprietary technique, "Gas Jet Deposition", has these capabilities and other advantages over established methods. In this technique, depositing atoms, molecules or clusters are "seeded" into a free jet which is directed at a substrate at low temperature in a "high" background pressure. The deposition rates can be exceptionally large; the "high" pressure, low temperature conditions permit the processing of new types of surfaces; and deposition can occur in a "reactive" mode for production of oxide and nitride materials. Phase I achievements include: (1) fabrication of uniform 100 layer alternating gold/copper thin film multilayer microstructures with 5 nm individual layer thickness; (2) fabrication of 3 nm gold particles; (3) deposition of copper oxide, gold oxide, silicon oxide and silicon nitride thin films. These results were confirmed using stylus profilometry, low angle x-ray diffraction, auger depth profiling, and transmission electron microscopy.
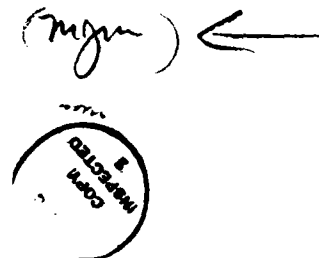
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ONR Final Report

Gas Jet Deposition of Multicomponent Ultrafine Microstructures

We proposed, in Phase I, to demonstrate the capability of our Gas Jet
Deposition technique for fabricating two kinds of ultrafine microstructures:

a) bimetallic multilayer films
b) dispersions of metal clusters in low conductivity matrices

The expectation is that such structures will exhibit useful and novel
electronic, magnetic, optical, and mechanical properties, and that, therefore,
any method capable of generating them in a simple and rapid manner is a method
of great utility.   In Phase I, we have indeed shown that GJD possesses that
utility.

In brief, we succeeded in fabricating several representative examples of
microstructures a) and b), and we characterized them with a number of
techniques.   We describe our apparatus, procedures and results for each in
Sections I and II below, showing why Gas Jet Deposition is a unique approach in
each case.

I Bimetallic Multilayer Films

We deposited microstructures consisting of alternating layers of Au and Cu
on a glass slide.   In our best samples, each layer was approximately 50A
thick, and there were 100 such layers covering an area of 2 cm x 1 cm. Before
describing the deposition apparatus and procedure we list the ways in which
the resulting microstructure was characterized:

a)   Stylus Profilometry: The average thickness was determined with a Sloan-
Dektak profilometer at 15 points across the film, and found to be 4996 A, with
no deviation from the average of more than 11 A.   From the measured film
thickness, and the known total number of layers, the individual layer
thickness is seen to be about 50 A.   A typical profilometer trace across an
incision in the metal film is shown in Fig. 1.

b)   Low angle X-ray scattering: At the suggestion of Dr. Donald Polk of ONR,
we asked Professor Frans Spaepen of Harvard University to carry out a low angle
X - ray scattering analysis of our multilayers.   The spectrum he obtained is
shown in Fig. 2a.   The absence of a second harmonic in this spectrum shows
that the layer profile is symmetric, ie, the layers are of equal thickness.
The third harmonic peak indicates that the layer boundaries are still sharp,
even though Au and Cu will interdiffuse.   By means of a preliminary spectral
simulation, Fig. 2b, Professor Spaepen found the layer thickness to be
60 A; this is in acceptable agreement with our own profilometer determination
of 50 A.

c)   Depth Profiling via AES and XPS. Professor Steven Suib of the University
of Connecticut, in a joint effort with Schmitt Technologies, has characterized
several of our samples by means of Auger electron spectroscopy, and X - ray
photoelectron spectroscopy. He reports two main findings. First, both AES
and XPS show the alternation of intensity that one would expect from well
defined metallic layers as seen in Fig.3, which was derived from XPS data. The

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oscillations in Au/Cu ratio do not appear to be high for these samples, but there are two reasons for this. The individual layer thickness in the sample analyzed by Professor Suib was less than 20 A. Since this thickness is of the same order as the depth resolution (electron escape depth) for AES and XPS, even sharp layers cannot be perfectly distinguished. In addition, Au and Cu are known to interdiffuse rapidly, and we expect that some interface smudging had occured between deposition and analysis.

Second, Professor Suib noted that, at least qualitatively, the interior of our Au/Cu composites showed a lower oxygen content than any other metallic films that he had analyzed. (Naturally a chemisorbed layer was present on the exposed top layer.) Although we cannot quantify this at present, it is an interesting result particularly since we took only elementary precautions to assure carrier gas purity. GJD is to some extent "self cleaning" since the high speed jet shields the substrate from downstream background contamination.

We discuss next the apparatus used to deposit Au/Cu, as well as other, bimetallic multilayers, since several important modifications and extensions were developed during Phase I.

The essential physics of the gas jet is as follows. A light carrier gas entrains metal atoms evaporated within the nozzle and transports them to the downstream substrate at sonic velocities. The flow is highly directional and the impact energy of the metal atoms can be controlled over a range of several electron volts. We did not need to make use of impact energy control in Phase I, although we will do so in Phase II. The directionality - which assures that every metal atom impacts on the substrate - is a useful feature of our method.

We deposited the Au - Cu multilayers on glass slides of an area (2 cm x 1cm) and the net result of our computerized process control strategy was a 5000 angstrom multilayer film of Au and Cu consisting of 100 alternating 50 angstrom layers of each metal, of uniform thickness, reasonably sharp interfaces, and (qualitatively) high purity. Despite the fact that Cu and Au comprise an "easy" system to work with, we regard this sample as evidence that fabrication of high quality multilayer structures of any pair of metals can be effectively carried out by Gas Jet Deposition.

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IIa   Deposition of Oxides

Although Phase I was only concerned with metallic layers, it is relevant to be able to convert those metallic layers rapidly into the corresponding oxides during the deposition process itself. In general, the ability to alternate metal and metal oxide layers is of intrinsic interest to us. In particular, is known that oxide layers can greatly improve the adherence of some metal films to a substrate; we wanted a means of assuring this for our multilayers, especially where gold was involved. In Phase I, we developed a novel and effective approach to high speed metal oxide formation, an approach made possible by the characteristic operating pressures in gas jet deposition. As one result, we are now able to routinely deposit highly adherent gold films. Another result is the formation of a hard adherent black film of Cu oxide. Professor Suib is currently analyzing the exact composition of this oxide. We tested its adherence by a Scotch tape test, and it was not at all removed. The film is even difficult to scratch with a metal needle.

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We were also able to radically enhance the adherence of _gold_ films by means of this oxygen treatment. We initially found, as have most other workers, that a gold film deposited directly on a glass substrate will not adhere, and will be removed easily and completely by a Scotch tape test. But we observe a spectacular effect on adherence when deposition of even just the first few atomic Au layers is oxidized. We duplicated the procedure for Cu oxide films described above, but simply turned off the oxidizer after the first few monolayers of Au were deposited. We then continued deposition until the total film thickness was about 2000 A. The resulting film was not removed by the Scotch tape test, and indeed was difficult to scratch off the glass even with a metal point. The reason for the improved adherence is that a thin layer of _gold oxide_ is formed in direct contact with the glass surface. This layer is actually visible when the gold film is viewed through the bottom of the glass slide; the coloration is strikingly different than that of metallic gold. Depending on oxide thickness we observe a range of colors from a vivid red bronze to a metallic blue. The oxide layer is too thin for interference effects, and the colors are likely connected with the presence of small nuclei of gold oxide particles of perhaps nanometer dimension. In any case, the effect on adherence of the gold film is quite decisive. What is important in our procedure is the tremendous efficiency of the GJD oxidation technique in bringing about improved adherence at low temperature. The fact that this can be accomplished for gold indicates the potential power of our approach. The drastic effect in the case of gold has a clear implication for other systems.

We found the same improvement in the adherence of _silicon_ films generated by by GJD nozzle. We deposited silicon with the oxidation process turned on for the first few seconds, thereby depositing several monolayers of silicon oxide. The oxidizing treatment was then turned off, while Si deposition continued. The result was a translucent yellow film of silicon on a small number of monolayers of silicon oxide. This film survived the Scotch tape test; without the oxidizing treatment, our experience has been that the silicon film adherence is poor.

Even more remarkable was the silicon _oxide_ film produced by operating the oxidizing process during the entire Si deposition run. The result was a completely transparent film of silicon oxide, about 1 micron thick as measured by profilometry, that was not removed by Scotch tape. Again it must be emphasized that this silicon oxide film was made at nearly room temperature. Professor Suib is now analyzing the oxide composition for us.

The simplicity with which oxidizing co-processing of depositing films can be combined with operation of a gas jet deposition source suggests that influence over many properties - in addition to adherence - will be easy for us to achieve. Indeed, we have also had success with the formation if silicon nitride films using a nitriding process similar to the oxidizing treatment.

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IIb   Ancillary Techniques

In the course of refining the process control for multilayer deposition, we developed several ancillary techniques that will be of future use in Gas Jet Deposition of multilayer structures.   For completeness, we describe them briefly.

1) A technique for vaporizing refractory metals.

High melting point metals are difficult to vaporize in a source such as that used for Cu and Au.   Yet bimetallic films involving refractories, eg W, Ta, Nb, would be of interest. We made some progress in developing a refractory metal vapor source that could be incorporated in a GJD nozzle assembly.   To date it has been used to deposit a faint W film in a short time.   In any case this device shows some promise as a small scale, general source of refractory (and perhaps other) metal vapors.

2) Jet control by auxiliary means.

We developed an auxiliary means to control the jet source.   In principle this enables us to:

1)   reduce film thickness and create a ribbon shaped deposit
2)   gasdynamically impose temporal variations on the deposition rate
3)   obtain a flat film over a large area

II Cluster Deposition in a Low Conductivity Matrix

We had originally planned to inject metal clusters into thin non-conducting films and into liquids. Because so much of our effort was devoted to developing thin film deposition techniques for multilayer fabrication, we elected to emphasize liquids in this part of our Phase I effort. We had several reasons for doing so. We already had preliminary experience with liquid injection, so that we knew we could make rapid progress. We had definite ideas on how to develop the technique and in actual applications for it. Moreover, we had recently been reading about the sol-gel technique for ceramic processing, and we discerned some interesting similarities between our method of producing aqueous metal colloids and the "nano - scale" sol - gel method.

We carried out injection into liquids with the same kind of gas jet source that we used for film deposition. The main difference is that liquids are used as the "deposition" target. Our first versions of the experimental apparatus were operated in a batch mode in which small amounts of metal, eg, gold, evaporated into the carrier jet, and injected into a fixed amount of liquid.

We developed our liquid injection method in several ways. First, we extended the range of receivers to liquids such as water, epoxy and glycerol. Second, we used a variety of metals other than gold, such as copper and platinum. Third, we tried out a preliminary continuous version of our apparatus rather than a batch process, a clear advantage for an actual production process.

We generated colloids of Au, Cu, and Pt in water, glycerol, and epoxy, under varying conditions of nozzle pressure, and at varying metal injection rates. The aqueous sols and those in glycerol were stabilized by addition of NaCl at a concentration of .1 millimoles /liter.

Photographs of several of these colloids were taken to document degradation over time. Many of the metal colloidal sols were stable over many weeks. The metal sols had the expected deep and vivid coloration. The color is characteristic of the particle diameter, and for the colloids we generated the particle size is small, eg, less than 10 nanometers. Fig. 4a shows an electron micrograph of gold clusters exposed by evaporating an aqueous gold colloid. The particle size is about 3 nanometers, and the size distribution is fairly uniform. Fig. 4b shows an aqueous gold colloid generated under somewhat different conditions. Although the clusters appear to be larger, they are actually composed of chains of 3 nanometer clusters. Thus our injection technique appears to favor a small cluster size.

The injection of gold atoms into liquid epoxy is particularly interesting. We were unable to obtain micrographs of that colloid since there is no way to evaporate epoxy and expose the clusters. However, the vivid wine red color matches that of our best aqueous gold colloids, for which a cluster size of 3 nm was determined by electron microscopy. In addition, we recorded a visible - U.V. absorption spectrum which exhibited a maximum at 530nm, consistent with a small cluster size. Thus, even though the physical properties of liquid

epoxy (viscosity, surface tension, dielectric constant) differ greatly from those of water, the cluster size produced by our injection method appears to be the same. We find similar results with glycerol as the receiving liquid.

The results of our experiments indicate that we can obtain clusters in the nanometer size range, with, apparently, a uniform size distribution, in liquids with very different properties. We do this with a method that is purely physical and applicable to virtually any metal, and, presumably, non - metals as well. The generality of this approach is distinctly advantageous for obtaining dispersions of ultra - fine particles. The gas jet injection approach provides a very unusual route to colloid production, one in which cluster size is probably determined by growth on a liquid surface rather than, as is more usual, within the body of the liquid.

We made an exploratory attempt to inject gold into molten salts, such as LiCl. We had no experience in handling molten salts, and we made little progress. Our main problem was that our apparatus was too small to handle the large heat dissipation needed to melt a volume of salt comparable to that of the aqueous colloids. At the time of this writing we are putting together a system of more convenient dimension. (We do not anticipate difficulty in the injection process per se.)

We hoped to demonstrate in this part of our Phase I effort that injection of atoms or small clusters into molten non-conducting media could be carried out in a general and continuous manner. We believe that our results indicate the feasibility of doing so, for almost any substance and any receiving liquid.
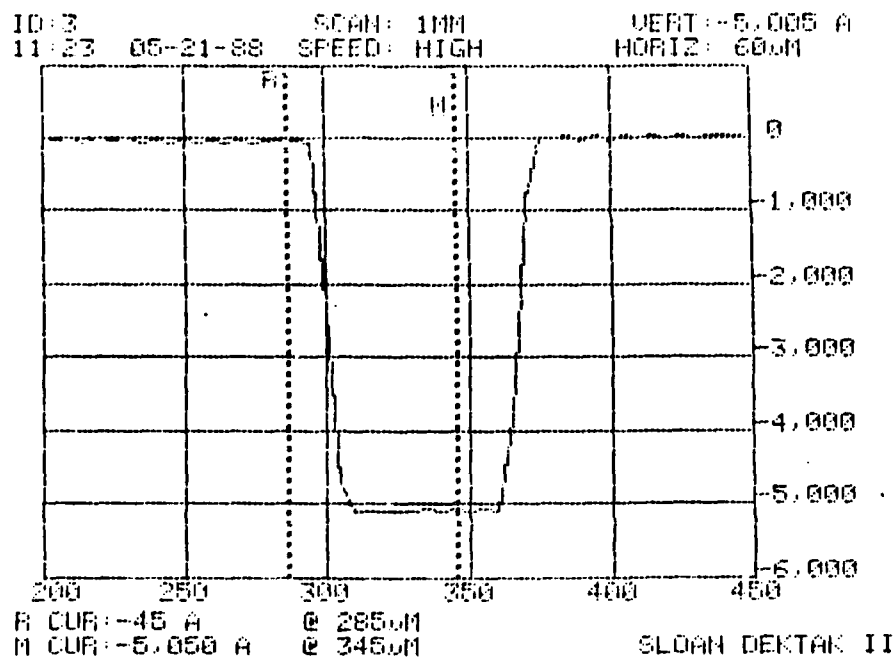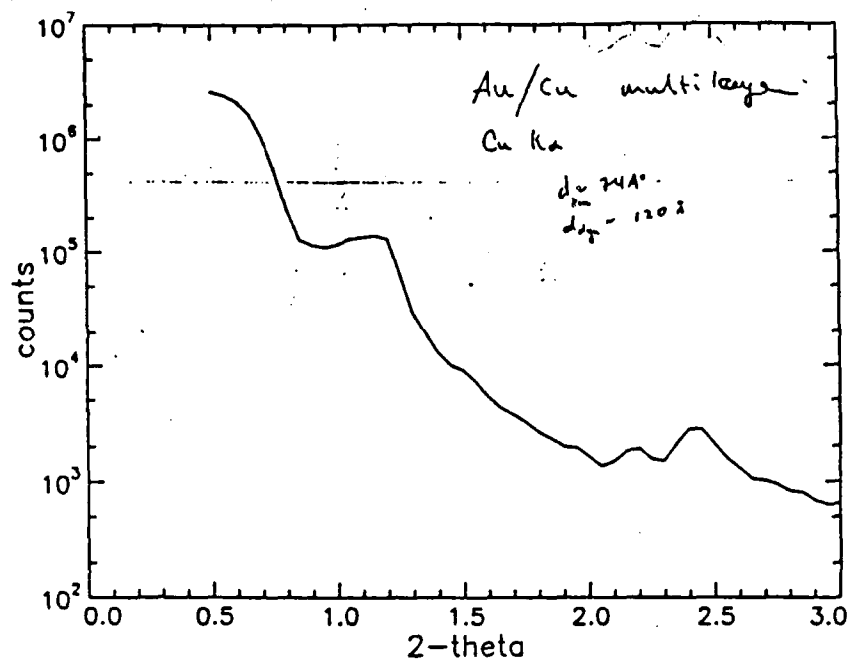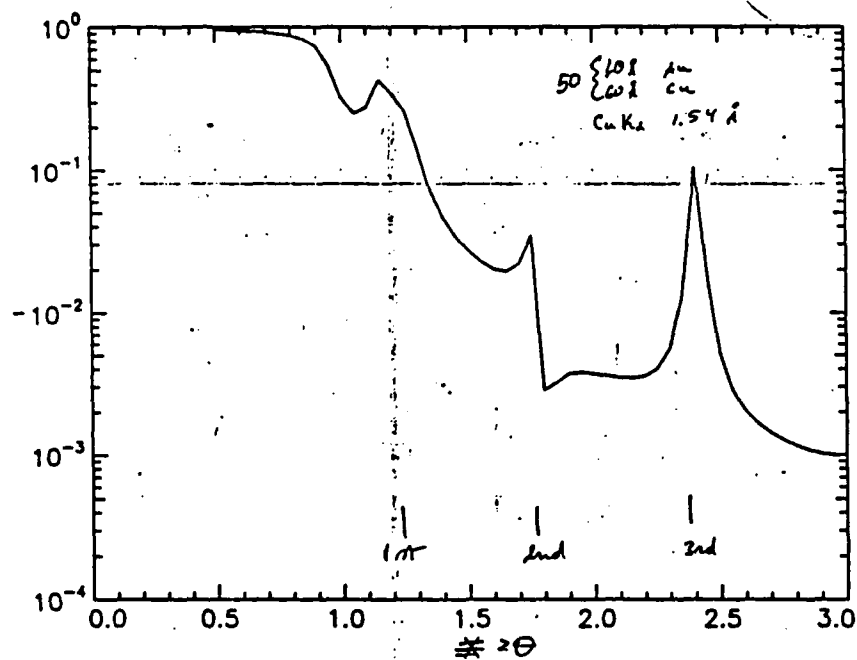
Figure 1. Profilometer trace across incision in Au - Cu multilayers. Depth = 5005 angstroms.

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a)   experimental data

b) simulation; 60 angstrom symmetric layers

Figure 2.   Low angle X - ray scattering from Au - Cu
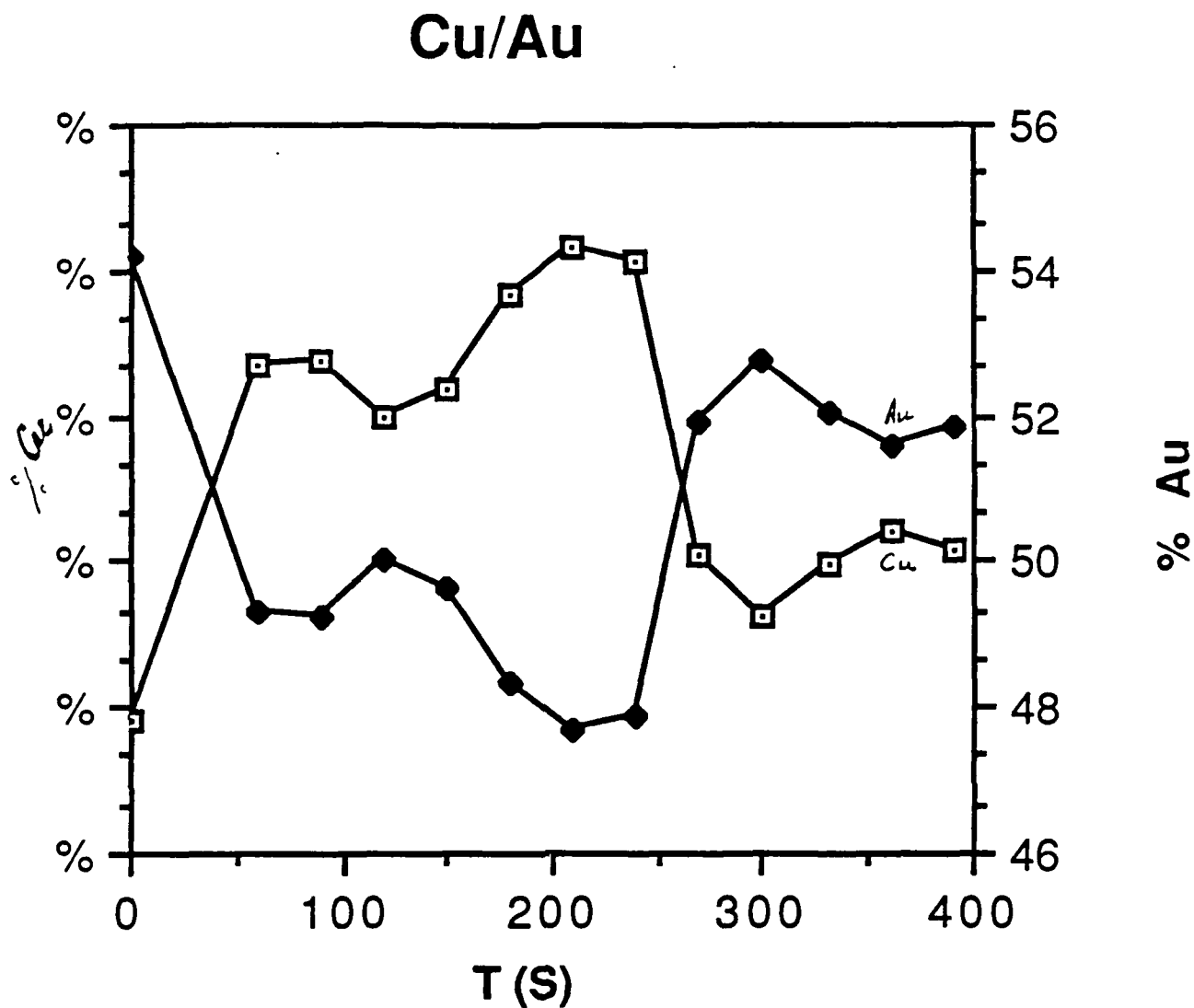multilayer microstructure:

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Cu/Au

Figure 3.   XPS "depth" profile: intensity vs sputtering time for a Cu – Au sample of about 20 angstrom layer thickness; absolute depths not known.

Fig. 4a. Transmission electron micrograph of Au colloid in water. Note the magnification of 31,000x which is given an additional factor of 2.7x by the print. Small dark spots are Au particles roughly 3nm in diameter. These particales are spherical -- the oblong shape is an artifact of motion during the exposure.
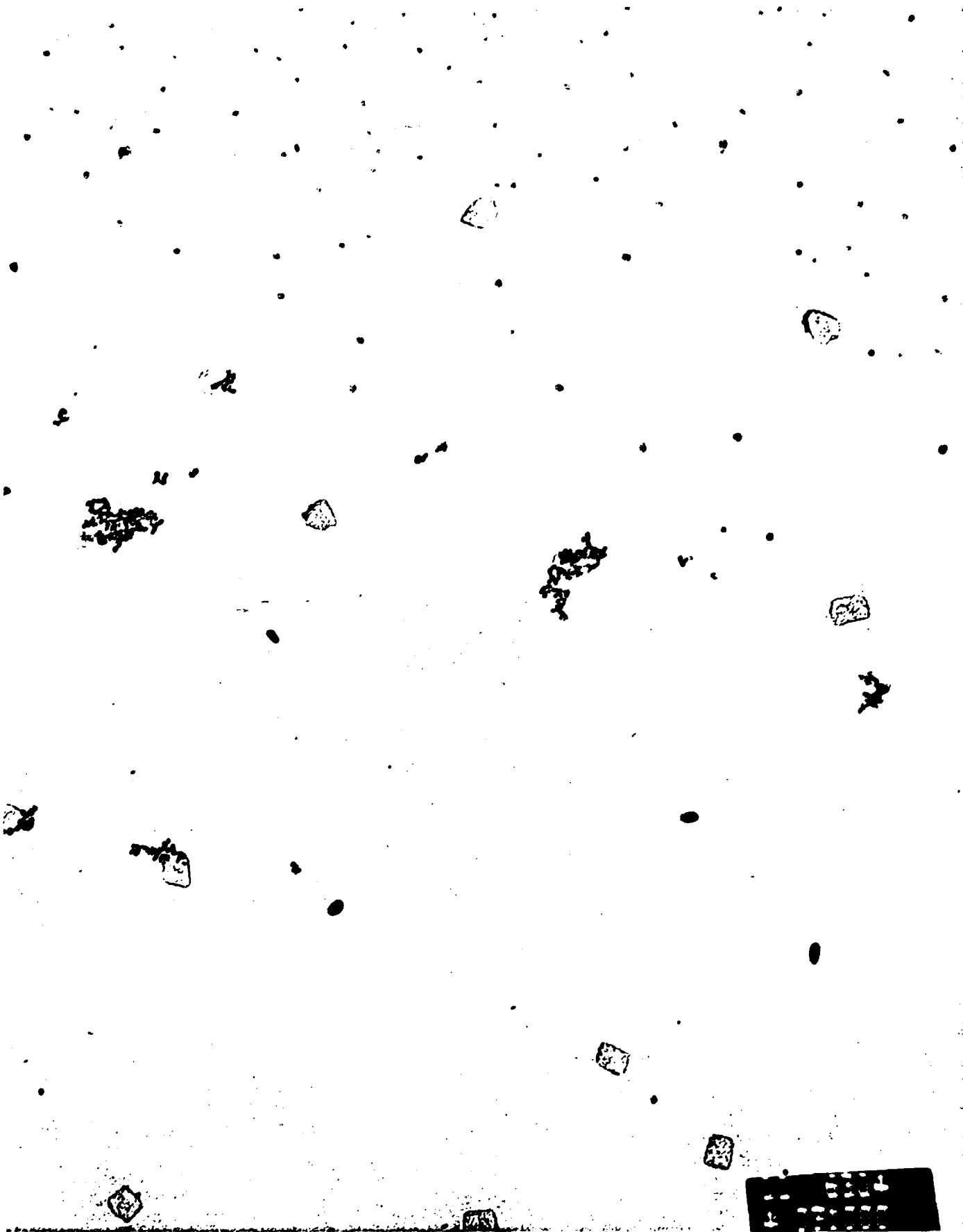
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Fig. 4b. Transmission electron micrograph of another Au colloid in water with higher Au concentration. As in Fig. 4a, the magnification is 31,000x with an additional factor of 2.7x in the print. Note that the larger particles appear to be agglomerations of individual smaller particles similar in size to those shown in Fig. 4a.