Tris(trimethylsilyl)arsine is a liquid with a relatively low vapor pressure (bp 50–52 °C at 10^{-3} mmHg)[12] and may prove useful as a safer alternative to AsH_3 gas in the vapor deposition of GaAs and other As containing alloys. Gallium trichloride has an appreciable vapor pressure at room temperature and has been applied to CVD growth of GaAs in other systems.[21] The extension of these preliminary results to vapor-phase epitaxy is worth investigating as an alternative to typical OMCVD processes.

(21) Rubenstein, M.; Myers, E. *J. Electrochem. Soc.* **1966**, *113*, 365.

Ultrasonic Irradiation of Copper Powder

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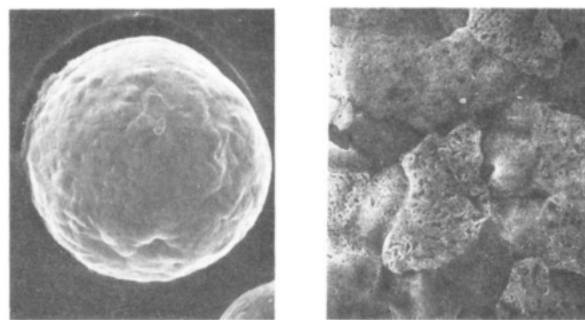*505 South Mathews Avenue, Urbana, Illinois 61801*
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Ultrasonic irradiation enhances the reactivity of metal surfaces. Because of this, the sonochemical activation of various metals has become a routine synthetic technique.[1-6] The mechanisms of heterogeneous sonochemistry, however, remain largely unexplored,[1,3,7,8] In comparison, a detailed understanding of the mechanism of *homogeneous* sonochemistry has recently been developed.[9,10]
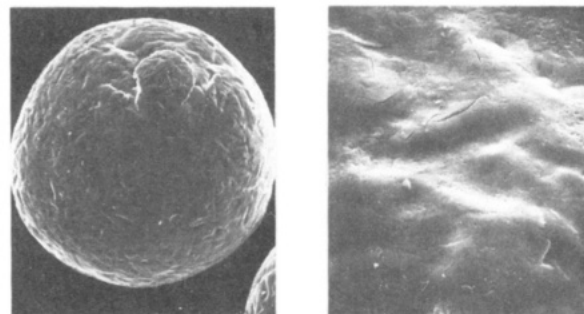
When a liquid is irradiated with high-intensity ultrasound, acoustic cavitation occurs.[1] If this formation, growth, and implosive collapse of bubbles takes place in a homogeneous liquid, intense local heating results and shock waves are produced. If it occurs near an extended liquids–solid interface, the collapse is extremely asymmetric and generates a high-speed jet of liquid directed at the surface.[11-13] Acoustic cavitation near a solid surface can create localized erosion, induce high-velocity interparticle collisions, cause fragmentation of brittle materials, and improve mass transport.

To more fully understand the origins of heterogeneous sonochemistry, we have examined the effects of ultrasonic irradiation on copper in terms of surface morphology, atomic composition, and reactivity. We report here that ultrasonic irradiation of Cu powder leads to substantial changes in all three areas. We believe that these effects are due to interparticle collisions driven by the shock waves created by the ultrasonic field: the origin of the enhanced chemical reactivity comes from the removal of the surface

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(1) *Ultrasound: Its Chemical, Physical and Biological Effects*; Suslick, K. S., Ed.; VCH Publishers: New York, 1988.
(2) Lindley, J.; Mason, T. J. *Chem. Soc. Rev.* **1987**, *16*, 275.
(3) de Souza-Baroza, J. C.; Petrier, C.; Luche, J. L. *J. Org. Chem.* **1988**, *53*, 1212.
(4) Suslick, K. S. *Adv. Organomet. Chem.* **1686**, *25*, 73.
(5) Suslick, K. S. *Mod. Synth. Methods* **1986**, *4*, 1.
(6) Boudjouk, P. *J. Chem. Educ.* **1986**, *63*, 427.
(7) Suslick, K. S. In *High Energy Processes in Organometallic Chemistry*; Suslick, K. S., Ed.; American Chemical Society: Washington, D.C., 1987; p 191.
(8) Suslick, K. S.; Casadonte, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 3459.
(9) Suslick, K. S.; Cline, Jr., R. E.; Hammerton, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 5641.
(10) Suslick, K. S.; Flint, E. B. *Nature* **1987**, *330*, 553.
(11) Lauterborn, W.; Hentschel, W. *Ultrasonics* **1985**, *24*, 59.
(12) Preece, C. M.; Hansson, I. L. *Adv. Mech. Phys. Surf.* **1981**, *1*, 199.
(13) Neppiras, E. A. *Phys. Rep.* **1980**, *61*, 159, and references therein.

BEFORE ULTRASONIC IRRADIATION

AFTER ONE HOUR ULTRASONIC IRRADIATION

AFTER FOUR HOURS ULTRASONIC IRRADIATION
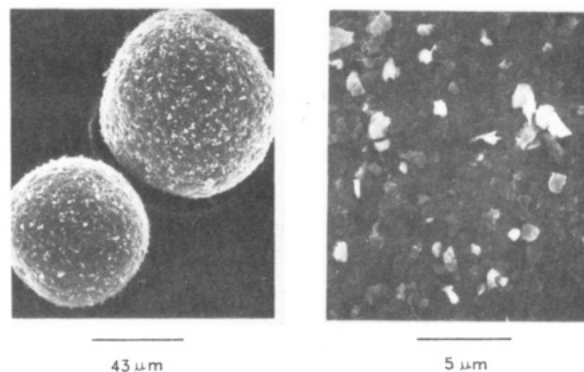

43 μm   5 μm

Figure 1. Effect of ultrasonic irradiation on surface morphology of 75-μm Cu powder. Note the increase of magnification of these scanning electron micrographs from left to right. SEMs were obtained on a Hitachi S-800 microscope.

oxide passivating layer and surface damage that these collisions induce.

In a typical reaction, 2.5 g of copper powder (Fischer, electrolytic purity) was loaded into a glass cell; ≈15 mL of dimethylformamide (DMF) was added under an Ar atmosphere and sparged. The slurry was then irradiated with ultrasound for various lengths of time at 15 °C. A Heat Systems-Ultrasonics W375 titanium immersion horn served as the ultrasonic source with acoustic intensities of ≈50 W/cm² at 20 kHz, as described elsewhere.[14,15] Degassed 2-iodonitrobenzene (10 mmol) was then added to the reaction cell after irradiation, together with a known amount of biphenyl as an internal GC standard. The

(14) Suslick, K. S.; Goodale, J. W.; Wang, H. H.; Schubert, P. F. *J. Am. Chem. Soc.* **1983**, *105*, 5781.
(15) Suslick, K. S.; Flint, E. B. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, D.C., 1987; p 195.

reaction vessel was heated with stirring to 100 °C under an Ar atmosphere, and aliquots taken for GC analysis of product (2,2′-dinitrobiphenyl) every 15 min, as shown in Figure 3. In separate experiments for surface analyses, the entire reaction cell assembly was transferred into a Vacuum Atmospheres inert-atmosphere box (<1 ppm O_2) after irradiation of the Cu powder. There the reaction solution was filtered, washed with tetrahydrofuran, and vacuum dried for >16 h at 80 °C. The surface was characterized by Auger electron spectroscopy (AES) and scanning electron microscopy (SEM).

The effects of ultrasound on the morphology of the copper powder are shown by the microphotographs of Figure 1. The gross morphology (particle size, degree of particle aggregation) is not changed significantly by even lengthy ultrasonic irradiation. The detailed surface morphology, however, is dramatically affected.

In some cases, the enhancement of heterogeneous reaction rates by ultrasound can be due simply to increased surface area of friable solids caused by shock fragmentation.[16,17] With large, thin flakes of Cu ($\approx$100 × 100 × 1 μm), this has been previously observed.[18] With the spherical metal powders used in this study ($\approx$75-μm diameter), however, fragmentation is less likely because of the higher structural strength of a sphere compared to a sheet. In fact, even 4 h of ultrasonic irradiation of 75-μm Cu powders decreases the particle size only slightly.

The effects of ultrasound on surface morphology are especially important in understanding the origins of heterogeneous sonochemistry. The Cu powder initially has a thick oxide coating with a distinctive texture (Figure 1), even before exposure to solvent. After 1 h of ultrasonic irradiation, the copper surface has been completely smoothed, as can be seen at the higher magnification. As demonstrated by AES, however, this surface is still completely copper oxide (see below). On close examination, cracking of the oxide layer is evident. After further irradiation, the oxide coating is completely removed, revealing a metallic surface with severe surface damage. It appears that the cracking of the oxide coating leads to its breaking off of the surface. In the SEMs, small pieces of the remnants of this oxide layer can be observed in Figure 1 (lowest right microphotograph).

The physical phenomena responsible for these effects include microjet formation, shock-wave deformation, and interparticle collisions. Microjet pitting is a well-known event with cavitation at *extended* surfaces.[12,13] At 20 kHz, however, the resonant bubble size has a diameter of more than 100 μm, and microjet formation will occur only with surfaces substantially larger than that.[12,13] A 75-μm copper particle, therefore, will *not* induce substantial deformation of a collapsing bubble. Shock-wave deformations are also important in metal surface erosion by cavitation, but no evidence for distortion of the originally spherical particles is seen in the SEM.

We have previously demonstrated the predominance of interparticle collisions (driven by the turbulence and shock waves created by the ultrasound) in the sonochemistry of fine nickel powders.[10] The surface smoothing, oxide removal, and subsequent surface damage are consistent with the effects expected from interparticle collisions. In contrast to small-diameter metal powders (<10 μm),[10] however, aggregation of larger particles does not occur upon
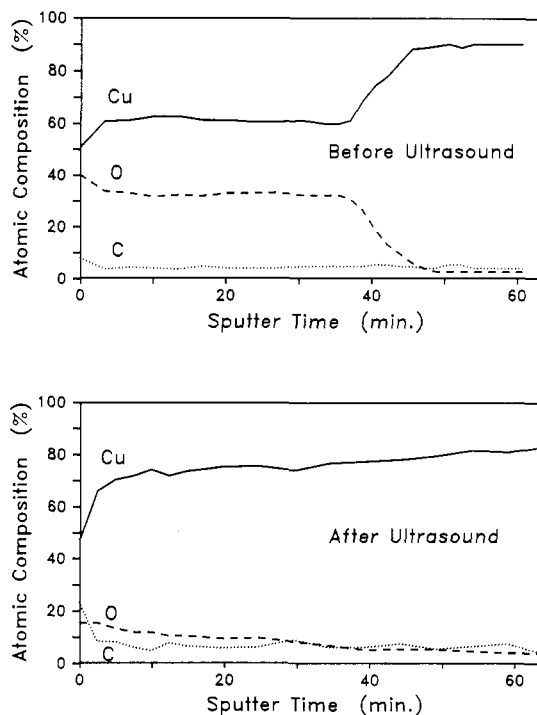
Figure 2. Surface composition depth profiles of 75-μm Cu powder. Depth profiles were derived from Auger electron spectra obtained on a Physical Electronics 595 Multiprobe spectrometer with Xe^+ sputtering at 3 keV. Sputtering times correspond to an erosion rate of $\approx$270 Å/min. The upper depth profile is of a Cu sample before ultrasound. The lower depth profile is of a Cu sample after 4 h of ultrasonic irradiation in dimethylformamide at 288 K.

ultrasonic irradiation. This is to be expected, since collisions between larger particles will be at lower speeds, insufficient to cause the localized melting necessary for agglomeration. Such collisions, however, are still capable of the removal of passivating oxide coatings and the creation of surface damage.

The changes in surface morphology are associated with dramatic changes in surface composition. Before ultrasonic irradiation of Cu powder, there is a thick and complete oxide (Cu_2O) coating. The oxide layer's thickness is $\approx$1.2 μm, as determined by AES depth profiles (Figure 2). After 1 h of irradiation, the oxide coating is still present with nearly the same thickness. After 4 h of irradiation, however, the oxide coating has been completely broken away.

On the surface of this newly exposed Cu, there is a thin ($\approx$300 Å) surface deposition of carbon. This carbon is *not* an artifact of the reaction workup or transfer: control reactions in which all manipulations are identical, but without the irradiation with ultrasound, do not leave any residual carbon. Ultrasonic irradiation of smaller particle Cu powders (average initial particle diameter $\approx$10 μm) also removes surface oxide and produces a very similar surface deposition of carbon. Carbon deposition occurs with ultrasonic irradiation in both decane and DMF. In DMF, small amounts (<10%) of surface nitrogen are also detected by AES. The origin of the surface carbon and nitrogen must be due to solvent decomposition at the active copper surface. We have previously demonstrated[19] the sonochemical cracking of alkanes under acoustic cavitation. Regardless of the detailed mechanism by which the carbon surface deposition occurs, it is clear that even low-reactivity liquids are not inert under sonochemical

(16) Suslick, K. S.; Casadonte, D. J.; Green, M. L. H.; Thompson, M. E. *Ultrasonics* **1987**, *25*, 56.

(17) Suslick, K. S.; Green, M. L. H.; Thompson, M. E.; Chatakondu, K. *J. Chem. Soc., Chem. Commun.* **1987**, 900.

(18) Lindley, J.; Mason, T. J.; Lorimer, J. P. *Ultrasonics* **1987**, *25*, 45.

(19) Suslick, K. S.; Grawienowski, J. W.; Schubert, P. F.; Wang, H. H.; *J. Phys. Chem.* **1983**, *87*, 2299.
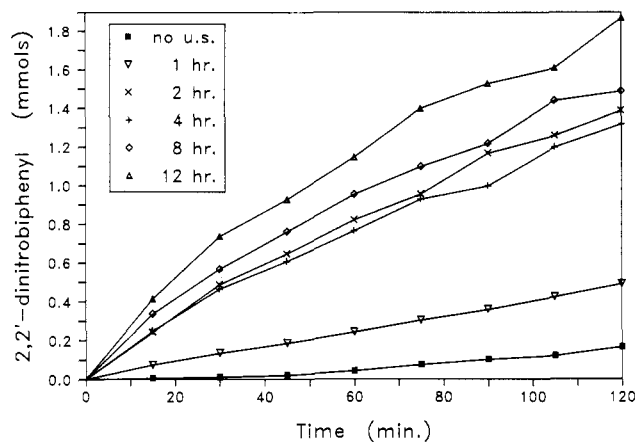
Figure 3. Initial rates of product formation in the Ullmann coupling reaction. The amount of 2-iodonitrobenzene is plotted against the length of ultrasonic pretreatment of Cu powder. Ultrasonic irradiation was done in dimethylformamide at 288 K with an acoustic intensity of ≈50 W/cm². Reactions were run at 373 K under Ar in dimethylformamide; 100% yield corresponds to 5.0 mmol.

conditions. Whether or not the surface deposition of carbon is important to the enhanced reactivity remains an open question. Further work is under way to clarify this matter.

The effects of ultrasound on the reactivity of Cu metal as a stoichiometric reagent have been documented in the literature in two cases: the Ullmann coupling[18] (where $C_6H_4(NO_2)$ is *o*-nitrophenyl)
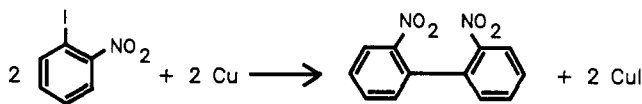
and the reaction of Cu with salicylalaniline to form uncharacterized copper complexes.[20] In the former case, substantial rate enhancements (as large as 64-fold) are reported when the entire reaction mixture is irradiated with ultrasound. This synthetically important rate increase was postulated to arise from multiple possible effects, including particle size reduction and surface cleaning. In addition, ultrasound has been used to enhance[21,22] the reduction of Cu salts by alkali metals to form highly reactive copper dispersions.[23]

To determine the effect of ultrasound on the reactivity of the copper surface, we choose to use the Ullmann coupling reaction as a kinetic probe. To this end, we irradiated a slurry of the copper powder *in the absence of substrate* (2-iodonitrobenzene) and then examined the rate of coupling upon addition of substrate. As shown in Figure 3, we find substantial rate enhancements upon ultrasonic pretreatment of the Cu powder. The induction period observed in the absence of ultrasound complicate a quantitative comparison of rates. At early stages of the reaction, pretreatment of Cu powder with ultrasound can increase rates more than 50-fold, while at later stages the rate increase is 10-fold. The effectiveness of pretreatment demonstrates that ultrasound produces an irreversible

change in the Cu powder (i.e., the removal of the oxide coating), even in the absence of substrate. Enhanced mass transport is *not* responsible for the sonochemical improvements.

In conclusion, ultrasonic irradiation of Cu powder removes the passivating oxide coating, induces significant surface damage, and enhances the reactivity of Cu powder. Interparticle collisions driven by shock waves are probably the causative event.

Chemical Vapor Deposition of Copper and Copper Oxide Thin Films from Copper(I) *tert*-Butoxide

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The low-temperature deposition of thin-film materials from molecular transition-metal precursors is an area of rapidly growing interest.[1-4] We now describe the deposition of copper-containing films from copper(I) *tert*-butoxide tetramer, $[Cu(O\text{-}t\text{-}Bu)]_4$,[5] which was chosen because it is one of the more volatile molecular derivatives of copper known. These results are related to efforts directed toward the chemical vapor deposition of thin films of the

(20) Kuzharov, A. S.; Vlasenko, L. A.; Suchkov, V. V. *Zh. Fiz. Khim.* **1984**, *58*, 542.

(21) Luche, J. L.; Petrier, C.; Gemal, A. L.; Zikra, N. *J. Org. Chem.* **1982**, *47*, 3806.

(22) Boudjouk, P.; Thompson, D. P.; Ohrbom, W. H.; Han, B. H. *Organometallics* **1986**, *5*, 1257.

(23) Rieke, R. D.; Burns, T. P.; Wehmeyer, R. M.; Kahn, B. E. In *High Energy Processes in Organometallic Chemistry*; Suslick, K. S., Ed.; American Chemical Society: Washington, D. C., 1987; p 223.

(1) (a) Girolami, G. S.; Jensen, J. A.; Pollina, D. M.; Williams, W. S.; Kaloyeros, A. E.; Allocca, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 1579–1580. (b) Kaloyeros, A. E.; Williams, W. S.; Allocca, C. M.; Pollina, D. M.; Girolami, G. S. *Adv. Ceram. Mater.* **1987**, *2*, 257–263. (c) Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643–1644.

(2) Gozum, J. E.; Pollina, D. M.; Jensen, J. A.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 2688–2689.

(3) (a) Rand, M. J. *J. Electrochem. Soc.* **1973**, *120*, 686–693. (b) Feurer, E.; Suhr, H. *Appl. Phys.* **1987**, *44*, 171–175. (c) Feurer, E.; Suhr, H. *Thin Solid Films* **1988**, *157*, 81–86. (d) Suhr, H.; Etspuler, A.; Feurer, E.; Oehr, C. *Plasma Chem. Plasma Proc.* **1988**, *8*, 9–17.

(4) (a) Czekaj, C. L.; Geoffroy, G. L. *Inorg. Chem.* **1988**, *27*, 8–10. (b) Trent, D. E.; Paris, B.; Krause, H. H. *Inorg. Chem.* **1964**, *3*, 1057–1058. (c) Truex, T. J.; Saillant, R. B.; Monroe, F. M. *J. Electrochem. Soc.* **1975**, *122*, 1396–1400. (d) Nash, B. D.; Campbell, T. T.; Block, F. E. U.S. Department of the Interior, Bureau of Mines, 1968, report 7112. (e) Aylett, B. J.; Colquhoun, H. M. *J. Chem. Soc., Dalton Trans.* **1977**, 2058–2061. (f) Aylett, B. J.; Tannahill, A. A. *Vacuum* **1985**, *35*, 435–439. (g) Rice, G. W.; Woodin, R. L. *J. Am. Ceram. Soc.* **1988**, *71*, C181–C183. (h) Gallagher, M. J.; Rhine, W. E.; Bowen, H. K. Proceedings of the Third International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites; Mackenzie, J. D., Ulrich, D. R., Eds.; Wiley: New York, 1987. (i) Bonetti, R.; Comte, D.; Hinterman, H. E. *Proc. Conf. Chem. Vap. Dep., Int. Conf., 5th* **1975**, 495.

(5) Although the vapor pressure of $[Cu(O\text{-}t\text{-}Bu)]_4$ has not been measured, it sublimes readily at 100 °C and 10^{-4} Torr. (a) Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, *94*, 658–659. (b) Greiser, T.; Weiss, E. *Chem. Ber.* **1976**, *109*, 3142–3146.