in NH_3 rules out investigation of charge trapping in this medium, but the cyclic voltammetry at negative potentials shows chemically reversible reduction in NH_3. Compared to the CH_3CN medium, the cyclic voltammogram in the NH_3 medium shows larger currents and less hysteresis.

Figure 1b illustrates the I_D–V_G characteristic[3,18,19] for poly(3-methylthiophene) in CH_3CN at -30 °C. The "charge trapping" observed in the cyclic voltammetry can be correlated with small changes in both the onset of conductivity (<100 mV) and magnitude of conductivity (~10–20%), but the essence of the I_D–V_G characteristic is illustrated in Figure 1b. We have discussed the I_D–V_G characteristic for positive V_G (oxidation) in previous reports.[3,18] Here we concentrate on the differences between the negative and positive V_G excursions. The maximum conductivity observed upon reduction is at least 100 times smaller than upon oxidation.[22] This is in rough agreement with the differences reported previously for reduced and oxidized polythiophene films.[6] The hysteresis for the negative scan of V_G is highly scan-rate dependent, while for the positive scan of V_G the hysteresis is largely insensitive to scan rate. This likely indicates slow charge compensation of the reduced polymer by the bulky $(n\text{-}Bu)_4N^+$ cation, especially at the reduced temperature employed for these experiments. Greater hysteresis is also expected for the more resistive form of the polymer.

Figure 1d shows the I_D–V_G characteristic in NH_3 at -55 °C. Compared to the CH_3CN results, the NH_3 data show a well-defined peak in conductivity at ~-1.5 V. The absolute conductivity in NH_3 appears to be higher than in CH_3CN, consistent with the greater amount of charge injected based on the differences in the cyclic voltammetry. The differences (kinetics and degree of reduction) in CH_3CN and NH_3 are likely attributable to differences in electrolyte used, but intrinsic differences in the two solvents may also play a role. We suggest that the observed increase and then decrease in conductivity of poly(3-methylthiophene) as it is reduced are due to partial filling and then complete filling of the conduction band, in analogy to previous work showing conduction to be greatly diminished by depleting the valence band of carriers.[3] The region of high conductivity of reduced poly(3-methylthiophene) appears to be ~1 V, ~0.3 V less than for the oxidized form of poly(3-methylthiophene), which has significantly higher maximum conductivity. This finding is consistent with the notion that higher conductivity is associated with greater delocalization in broader bands.[23]

The ruggedness of reduced poly(3-methylthiophene) in NH_3 at low temperature allows investigation of its optical properties on an optically transparent electrode.[24] The neutral form of the polymer in NH_3 at -33 °C shows an absorbance maximum at 486 nm, as reported for measurements in CH_3CN.[25] Upon reduction the 486-nm absorption declines, and there is growth in absorption in the near-IR with reasonable preservation of an isosbestic point at ~600 nm upon reduction to -1.8 V. These spectral changes are very similar to those found upon *oxidation* of the polymer in CH_3CN.[25] Oxidized and reduced polythiophene are also reported to have similar optical properties.[6] Similarity in the optical properties of the oxidized and reduced forms of the polymers is surprising. Studies are under way to examine the optical properties for the entire range of potentials where poly(3-methylthiophene) is durable, to determine the nature of differences in optical properties of the fully reduced and fully oxidized materials.

To summarize our new findings, low-temperature, nonaqueous media can be used to study the reduced form of poly(3-methylthiophene) revealing a finite potential region of high conductivity, ~1 V, centered at ~-1.5 V. The maximum conductivity is at least 100 times less than that of the oxidized form when measured in CH_3CN/0.1 M $[(n\text{-}Bu)_4N]BF_4$ at -30 °C. In NH_3/0.1 M KCF_3SO_3 at -55 °C the maximum conductivity of the reduced form is higher than in CH_3CN. The optical spectrum of reduced poly(3-methylthiophene) in NH_3 is similar to that of the oxidized form in CH_3CN. Further studies of poly(3-methylthiophene) and derivatives shown to be durable upon reduction will be reported subsequently.

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(22) The resistance of the leads of the electrode array used for these experiments had a measured resistance of 16 Ω. Therefore, the maximum I_D that we measure for oxidized poly(3-methylthiophene) reflects mainly the resistance of the leads, whereas the maximum I_D for the reduced polymer reflects mainly the resistance of the polymer.

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Use of Tris(trimethylsilyl)arsine To Prepare Gallium Arsenide and Indium Arsenide

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One of the processes commonly used for the epitaxial growth of GaAs and other compound semiconductors is organometallic chemical vapor deposition (OMCVD).[1] For GaAs, it has been the general practice to utilize a trialkylgallium compound and AsH_3 in this process, as exemplified by eq 1. However, concerns regarding the use

$$Me_3Ga + AsH_3 \xrightarrow[\sim 700\ ^\circ C]{H_2} GaAs + 3MeH \qquad (1)$$

of AsH_3 have prompted a number of researchers to evaluate other sources of arsenic; thus, replacements for AsH_3 that have been studied include As, Me_3As, Et_3As, Et_2AsH, and t-$BuAsH_2$.[2] Alternatively, some adducts of gallium and arsenic compounds,[3-5] as well as a monomeric and a dimeric mono(arsino)gallane,[6,7] have been used as single-source GaAs precursors.

Recent research in our laboratories has demonstrated that dehalosilylation reactions (e.g., eq 2) are a facile route

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$$R_2AsSiMe_3 + GaX_3 \rightarrow \tfrac{1}{3}(R_2AsGaX_2)_3 + Me_3SiX \quad (2)$$
$$R = Me_3SiCH_2,\ X = Cl \text{ or } Br$$

to the formation of the Ga–As covalent bond, and as a result we have prepared and characterized a number of new Ga–As compounds.[8-11] We now report the first examples of the use of dehalosilylation reactions to prepare GaAs and InAs. Reactions between $(Me_3Si)_3As$ and MX_3 (M = Ga, X = Cl or Br; M = In, X = Cl) proceed at relatively low temperatures to eliminate Me_3SiX with the concurrent formation of GaAs and InAs, respectively (eq 3).

$$(Me_3Si)_3As + MX_3 \rightarrow MAs + 3Me_3SiX \quad (3)$$
$$M = Ga,\ X = Cl \text{ or } Br;\quad M = In,\ X = Cl$$

Tris(trimethylsilyl)arsine[12] (0.343 g, 1.16 mmol) was added to a solution of $GaCl_3$ (0.205 g, 1.16 mmol) in 25 mL of ligroin (bp 90–110 °C) at room temperature.[13] Upon mixing, a white precipitate formed which quickly changed color to yellow then to orange. After stirring for 3 days at 75 °C, the volatiles were distilled off and shown to contain 2.89 mmol of Me_3SiCl.[14] The remaining brown solid was heated in the absence of solvent by using a heating mantle while the reaction bulb was opened to a −196 °C trap on the vacuum line. As the temperature was increased to 85 °C, a small amount of colorless material began to collect in the trap. The bulb was further heated at 125 °C for 30 min, and then the temperature was increased to 185 °C for 2 h. At this time it did not appear that any more material was collecting in the trap. The solid in the flask was dark brown to black. The colorless liquid was distilled from the trap and shown to contain 0.39 mmol of Me_3SiCl (total Me_3SiCl = 3.28 mmol, 94% theoretical). Further heating of the solid product to 380 °C for 90 min resulted in a trace of yellow liquid collecting in the trap beginning at 330 °C. The resulting black solid (0.136 g, 81% yield) was poured out of the bulb through the valve stem. It was shown to be GaAs of about 95% purity by partial elemental analysis[15] and comparison of its X-ray powder diffraction pattern with that for a bona fide sample of GaAs. In a separate experiment, $GaCl_3$ (0.411 g, 2.33 mmol) and $(Me_3Si)_3As$ (0.688 g, 2.33 mmol) were combined in pentane (30 mL). A precipitate formed as in the first experiment. The mixture was stirred overnight at room temperature, and the precipitate appeared light brown. Removal of volatiles showed that 4.47 mmol of Me_3SiCl had formed. Toluene (30 mL) was distilled onto the brown solid, and the slurry was stirred overnight at 90 °C, causing the formation of an additional 1.42 mmol of Me_3SiCl. The resulting solid was heated in the absence of solvent overnight at 140–160 °C and then for 3 h at 160–180 °C. An additional 0.60 mmol of Me_3SiCl was formed (total Me_3SiCl = 6.49 mmol, 93% theoretical). The bulb containing the solid was heated with a cool flame (propane, no oxygen; ~400–500 °C) for 2 h, and a trace of yellow liquid collected in the trap. The resulting black solid (0.294 g, 87% yield) was shown to be GaAs of about 96% purity by complete elemental analysis[16] and comparison of its X-ray powder diffraction pattern with that for a bona fide sample of GaAs.

The reaction between $(Me_3Si)_3As$ and $GaBr_3$ did not proceed as readily as the corresponding reaction with $GaCl_3$. Stirring an equimolar mixture of $(Me_3Si)_3As$ and $GaBr_3$ (1.19 mmol) overnight in benzene at 47 °C resulted in the elimination of 1.39 mmol of Me_3SiBr; an additional 1.16 mmol of Me_3SiBr was eliminated after heating overnight at 75–85 °C. Further heating of the resultant reddish-brown solid in the absence of solvent to 410 °C did not result in the clean elimination of additional Me_3SiBr; rather, the formation of an unidentified slightly volatile yellow liquid was observed. The nonvolatile black solid was shown to be GaAs of 88% purity by partial elemental analysis[17] and comparison of its X-ray powder diffraction pattern with that for a bona fide sample of GaAs. The ^1H NMR spectrum of the yellow liquid consists of broad peaks near 1 ppm.

The reaction of $(Me_3Si)_3As$ with $InCl_3$ proceeded in a manner similar to the analogous reactions with gallium halides. $InCl_3$ (0.314 g, 1.42 mmol) and $(Me_3Si)_3As$ (0.415 g, 1.41 mmol) were combined in 35 mL of pentane. A salmon-colored precipitate formed immediately upon mixing and rapidly changed color to dark brown. The mixture was stirred at room temperature for 3 days, and 2.33 mmol of Me_3SiCl evolved. Further heating in benzene at 70–75 °C for 4 days resulted in the formation of an additional 0.99 mmol of Me_3SiCl. Heating of the remaining brown solid in the solid state overnight at 150 °C caused the elimination of 0.32 mmol of additional Me_3SiCl. Finally, the solid was heated for 15 min with a cool flame, and a trace (0.05 mmol) of Me_3SiCl collected in the trap (total Me_3SiCl = 3.69 mmol, 87% yield). The resulting fluffy black solid (0.153 g, 57% yield) was shown to be InAs of 98% purity by complete elemental analysis[18] and comparison of its X-ray powder diffraction pattern with that for a bona fida sample of InAs.

This work demonstrates that dehalosilylation reactions provide a viable route to the formation of GaAs and InAs. These two compound semiconductors were isolated in 88–96% and 98% purity, respectively, from very crude experiments with no attempts to optimize the reaction conditions. The formation of GaAs and InAs with low incorporation of Si relative to C and to halogen in these experiments is of interest. This may be due to the decomposition of the Me_3Si group to form polysilanes at elevated temperatures. During the thermal decomposition of $(Me_3Si)_3Al$ polysilanes have been observed;[19] similar decomposition of the Me_3Si group may occur at high temperatures in our system. In contrast, the pyrolysis of $[(Me_3Si)_2AlNH_2]_2$ gave a solid solution of AlN and SiC.[20]

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(14) The quantities of Me_3SiCl or Me_3SiBr formed in the reactions were determined as HCl or HBr by vacuum distillation of all volatiles from the reaction mixture followed by hydrolysis and titration with standard NaOH solution.
(15) Anal. Calcd (found) for GaAs: C, 0.00 (1.35); H, 0.00 (0.98); Cl, 0.00 (2.36); Si, 0.00 (0.45).
(16) Anal. Calcd (found) for GaAs: C, 0.00 (1.68); H, 0.00 (0.30); As, 51.80 (50.08); Cl, 0.00 (2.51); Ga, 48.21 (45.96); Si, 0.00 (0.51); (Ga:As mole ratio = 1.00:1.01).
(17) Anal. Calcd (found) for GaAs: C, 0.00 (3.58); H, 0.00 (0.19); Br, 0.00 (7.21); Si, 0.00 (<0.7).
(18) Anal. Calcd (found) for InAs: C, 0.00 (0.56); H, 0.00 (0.17); As, 39.49 (38.32); Cl, 0.00 (0.80); In, 60.51 (59.21); Si, 0.00 (<0.1); (In:As mole ratio = 1.00:0.99). The low yield of both InAs and Me_3SiCl obtained in this experiment may be due to the fact that a significant amount of material adhered to the walls of the reaction bulb and was not isolated.
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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.

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Ultrasonic Irradiation of Copper Powder

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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 oxide passivating layer and surface damage that these collisions induce.

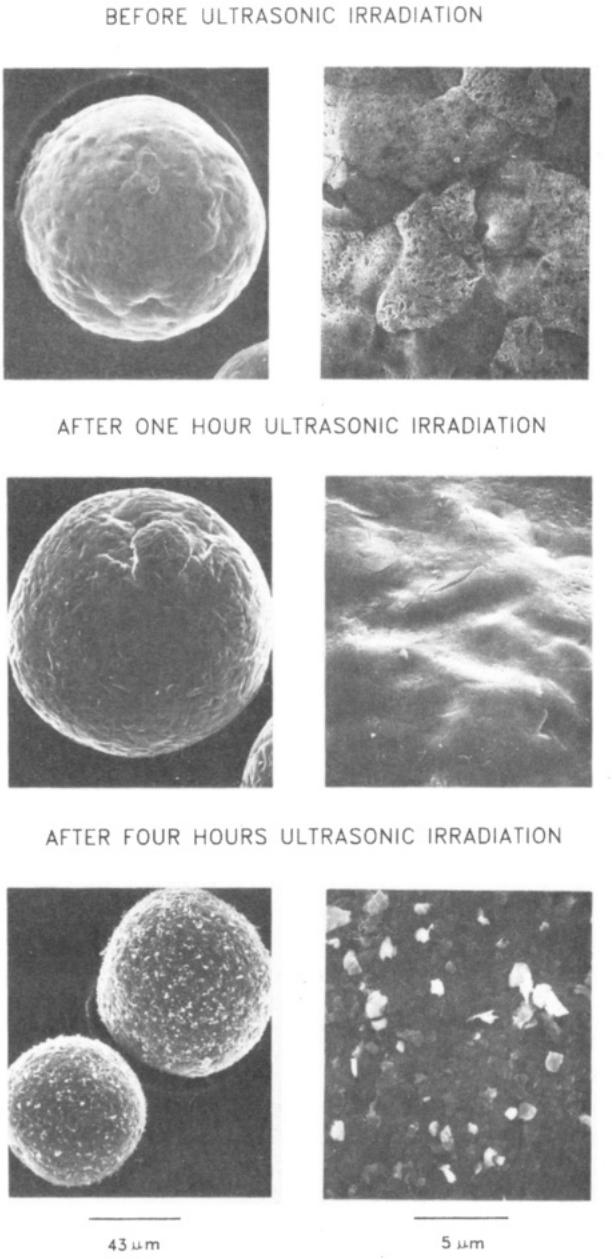

Figure 1. Effect of ultrasonic irradiation on surface morphology of 75-μm Cu powder. Note the increase of magnification of these scanning electron micrographs from left to right. SEMs were obtained on a Hitachi S-800 microscope.

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/cm^2 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

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